PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

# Ferroelectric phase transition of $S_{0.91}O_{0.09}C(NH_2)_2$ in electric fields

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(Received 19 April 1993)

Birefringence and dielectric studies on urea-doped thiourea, $S_{0.91}O_{0.09}C(NH_2)_2$, have been performed under a dc electric field. For the mixed crystal, no anomalies related to the transitions to intermediate commensurate phases of $\delta=\frac{1}{8}$ and $\frac{1}{9}$ are observed, indicating that the commensurate phases are suppressed by urea impurities. When a bias field is applied to the sample the dielectric-constant anomaly related to the ferroelectric phase transition splits into two peaks. One peak at a temperature $T_{c2}\approx 169$ K shifts driving the heating process to higher temperature with $dT_{c2}/dE\approx 0.9$ K/(kV/cm) while the other peak remains nearly fixed at $T_{c1}\approx T_{c2}(E=0)$ regardless of the electric field $E$. The field-induced phase between the $T_{c1}$ and $T_{c2}$ is attributable to the coexistence of ferroelectric and incommensurate phases.

## I. INTRODUCTION

Thiourea, $SC(NH_2)_2$, is a well-known ferroelectric material with an incommensurate ($I$) phase. It undergoes a second-order phase transition from a paraelectric ($P$) phase to an intermediate modulated phase at $T_i=202$ K and undergoes a first-order transition at $T_c=169$ K from the modulated phase to a ferroelectric phase with spontaneous polarization directed along the crystalline $a$ axis. The modulated phase includes two commensurate ($C$) phases of $\delta=\frac{1}{9}$ and $\frac{1}{8}$ as well as an $I$ phase with the modulation wave vector $\mathbf{q}=\delta\mathbf{b}^*$, where $\mathbf{b}^*$ is a reciprocal vector of the crystalline axis. In particular, the eightfold $C$ phase becomes stable under electric field.

Defects in crystals can play an important role in the properties of the $I$ phase. Thermal hysteresis and kinetic behaviors, such as memory effect, are closely related to defects which interact with modulation wave of the crystal. Detailed experimental and theoretical studies on the effects of defects for the $I$ phase have been carried out. Recently, Yoon and co-workers[1,2] have reported impurity effects on the modulated phases and on the phase-transition properties of urea-doped thiourea. It is claimed that the urea impurity disturbs especially the $C$ phases of thiourea.

In general the ferroelectric phase becomes more stable in the electric field and the ferroelectric transition temperature is increased with the electric field. For thiourea, the ferroelectric transition temperature $T_c$ is increased with $dT_c/dE\approx 0.9$ K/(kV/cm) when the electric field is applied along the $a$ axis. This has been studied extensively by dielectric constant, birefringence, and $x$-ray-scattering measurements, etc.[3-5] On the other hand, there are several reports[6-8] for $Rb_2ZnCI_4$, $Rb_2ZnBr_4$, and KDP showing that the transition revealed by the permittivity maximum splits into two under the electric field. One of the two permittivity maxima shifts to higher temperature with the field but the other one is located at fixed temperature irrespective of the field. Kroupa *et al.* proposed[7] the formation of a defect density wave in order to explain the phenomenon for $Rb_2ZnBr_4$, however, the phenomenon is not well understood.

In this work we examine the electric-field effect, as well as the impurity effect, on the formation of modulated phases and the ferroelectric phase-transition properties of $S_{0.91}O_{0.09}C(NH_2)_2$ by birefringence and low-frequency dielectric-constant measurements. The intermediate $C$ phases are completely suppressed by the urea impurity. Splitting in the ferroelectric transition behavior is also observed for this sample under electric field. It is interesting to see that there has been on report on such phenomenon for the pure thiourea.

## II. EXPERIMENT

Single crystals of $S_{0.91}O_{0.09}C(NH_2)_2$ are grown by slow evaporation of mixed solution, 50% $SC(NH_2)_2$ and 50% $OC(NH_2)_2$ in ethanol, at 30 °C. Urea, $OC(NH_2)_2$, is not a ferroelectric material but its molecular structure is similar to $SC(NH_2)_2$. The single crystal of urea-doped thiourea has similar morphology to that of the pure crystal and possesses the same cleavage planes. The urea molecules doped to the crystal are expected to act as pinning centers because they would break the local symmetry of the crystal. There has been a report showing that the urea impurity affects mostly the hydrogen bonds in thiourea crystal.[9]

The concentration of urea in the sample is found by gas chromatography after combustion using an element analyzer (Carlo Erba 1108). The samples have a cleavage plane normal to the ferroelectric $a$ axis. Cleaved samples with typical size of $3\times 3$ mm$^2$ area and 0.5 mm thickness are used in this work.

The complex dielectric constants ($\varepsilon_a'$ and $\varepsilon_a''$) and linear birefringence (LB) $\Delta n_{bc}=n_b-n_c$, where $n_b$ and $n_c$ are the refractive indices along the $b$ and $c$ axis, respectively, are measured simultaneously as the functions of tempera-

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ture. The dielectric constants are measured using an automatic bridge (HP 4275A LCR meter) with ac probing voltage of 0.1 $V_{pp}$. The LB is measured by the Senarmont method with wavelength of $\lambda = 6328$ Å. LB reflects the anisotropic structural changes and is related to polarization $P$, i.e., $\Delta n_{bc} = g_{bc} \langle P^2 \rangle + (\Delta n_{bc})_0$, where $g_{bc}$ is the polarization-optic coefficient, $(\Delta n_{bc})_0$ is the thermo-optic contribution, and $\langle\ \rangle$ denotes the configurational average. This relation has been applied to thiourea.[10] Semitransparent conducting indium-tin oxide electrodes are coated to the cleaved (100) faces in order for the light to pass through the electrodes. The dc electric field is applied along the ferroelectric $a$ axis.

## III. RESULTS AND DISCUSSION

The temperature dependencies of $\varepsilon_a'$ and $\Delta n_{bc}$ for undoped thiourea are shown in Fig. 1(a). The anomalies in $\varepsilon_a'(T)$ of $SC(NH_2)_2$ are related to the transitions from the $P$ phase to $I$ phase at 200.4 K ($T_i$), $I$ phase to the eightfold $C$ phase at 178 K ($T_8$), $I$ phase to the ninefold $C$ phase at 171 K ($T_9$), and the ninefold $C$ phase to the ferroelectric phase at 169 K ($T_c$). The dielectric anomaly at $T_x = 161$ K does not represent a phase transition. It can be due to an anomalous temperature dependence of the domain-wall density,[11] although there remain ambiguities in the origin of the dielectric anomaly. LB results of $SC(NH_2)_2$ show three anomalies representing the phase transitions of second order at $T_i$ and first orders at $T_9$ and $T_c$. LB does not show any anomaly related to the transition to $C$ phase of $\delta = \frac{1}{8}$ at $T_8$, since it is unstable in zero field. The existence of the $C$ phase was verified by LB measurement under electric field.[12] Our LB measurement shows a linear temperature dependence of $\Delta n_{bc}$ in the $C$ phase of $\delta = \frac{1}{9}$ as reported.[10] Thermal hysteresis in LB measurements is observed in a narrow temperature range near $T_c$, while that of dielectric constant occur over a wide temperature range between $T_c$ and $T_8$.

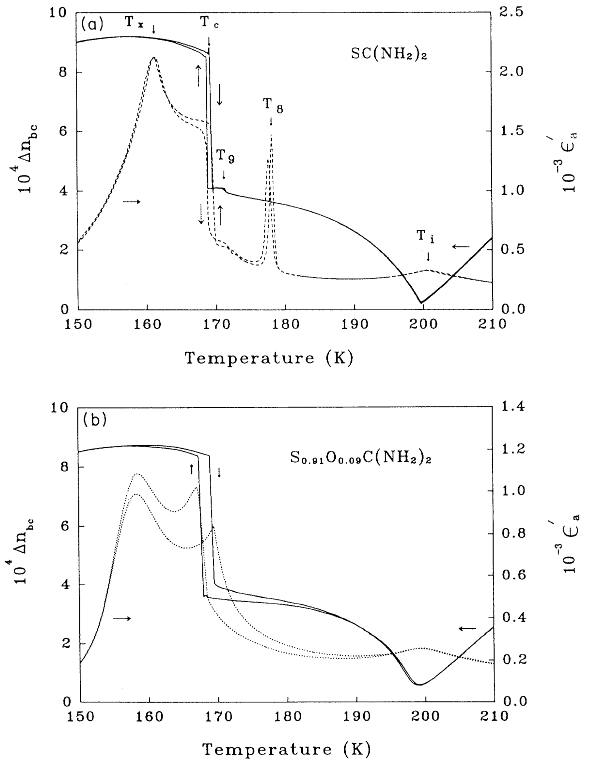

FIG. 1. (a) The temperature dependencies of $\varepsilon_a'$ (dashed line) and $\Delta n_{bc}$ (solid line) of $SC(NH_2)_2$ measured during the cooling and heating processes. (b) The temperature dependencies of $\varepsilon_a'$ (dashed line) and $\Delta n_{bc}$ (solid line) of $S_{0.91}O_{0.09}C(NH_2)_2$ measured during the cooling and heating processes.

Fig. 1(b) shows the temperature dependencies of $\varepsilon_a'$ and $\Delta n_{bc}$ for urea-doped thiourea, $S_{0.91}O_{0.09}C(NH_2)_2$, in zero field. The dielectric behavior of $S_{0.91}O_{0.09}C(NH_2)_2$ is very different from pure thiourea. $\varepsilon_a'(T)$ does not show a discontinuous behavior near $T_c$ but increases smoothly as temperature approaches $T_c$. Also there is no dielectric anomaly related to the transitions to the $C$ phases of $\delta = \frac{1}{8}$ or $\delta = \frac{1}{9}$. It seems that the impurities significantly affect the stability of the intermediate $C$ phases of thiourea. Random fields and pinning potential generated by the impurities can destroy the $C$ ordering by disturbing the periodicity of modulation wave. The thermal hysteresis near $T_c$ and in the $I$ phase is enhanced over the undoped crystal due to the impurity pinning effect as in the case of $(Rb_{1-x}K_x)_2ZnCl_4$ system.[13] The LB of $S_{0.91}O_{0.09}C(NH_2)_2$ does not show an anomaly nor the characteristic linear temperature dependence related to the transition to $\delta = \frac{1}{9}$ $C$ phase, which is consistent with the dielectric measurements. Urea impurity in thiourea crystal suppresses the intermediate $C$ phases of $\delta = \frac{1}{8}$ and $\frac{1}{9}$ while it renders the $I$ phase remain relatively stable. The dielectric behavior of $S_{0.91}O_{0.09}C(NH_2)_2$ can be described by a simple phenomenological theory[14] without the Umklapp terms. Moreover, the LB data do not show any indication of transition to the field-induced $\delta = \frac{1}{8}$ $C$ phase even with the electric-field strength up to 20 kV/cm. It has been reported that, for unrea-doped thiourea, there exists a critical field below which $\delta = \frac{1}{8}$ $C$ phase is unstable. The critical field strength becomes increased with the urea concentration.[1]

For the external bias field effects, the temperature dependence of $\varepsilon_a'$ at several field strengths is shown in Fig. 2. The temperature $T_{c2}$ at which the dielectric constant peak is located shifts to higher temperature at the rate of $dT_c2/dE \approx$ 0.9 K/(kV/cm) with the field. The $dT_c2/dE$ is nearly the same as $dT_c/dE$ of the pure thiourea although $T_{c2}$ itself is not the same as $T_c$ of the pure thiourea. Another distinct peak in $\varepsilon_a'(T)$ becomes apparent with increasing the bias field. The temperature of this second peak remains nearly fixed at $T_{c1} \approx T_{c2}(E=0)$ even with the increased electric field. This result is similar to what is observed in $Rb_2ZnCl_4$, $Rb_2ZnBr_4$ and KDP.[6-8] The splitting of phase-transition temperatures by electric field should be related to the defects induced by the doped urea impurities, since pure thiourea does not show the phenomenon.

To explain the splitting of the phase-transition temper-

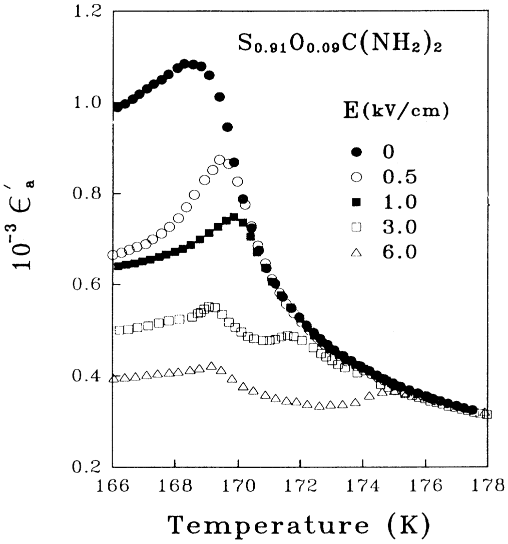

FIG. 2. The temperature dependence of $\varepsilon'_a$ near $T_c$ under the electric field.

ature by external field the LB data are simultaneously measured and compared. Figure 3 shows the field dependence of $\Delta n_{bc}$ as a function of temperature. The temperature of the discontinuous jump in $\Delta n_{bc}$ does not change for low electric field, $E \leq 1$ kV/cm, in contrast to the dielectric measurement. For $E=3$ kV/cm the $\Delta n_{bc}$ shows broad variations with considerable amount of tail, instead of a single jump, between the temperatures $T_{c1}$ and $T_{c2}$ during heating process. Upon further increase in the bias field, a discontinuous behavior is recovered and the major change in $\Delta n_{bc}$ occurs near the $T_{c2}$ of the dielectric measurement. The LB behavior with $E=6$ kV/cm is similar to the pure thiourea except a shift in $T_c$ and a small jump in $\Delta n_{bc}$ near $T_{c1}$. The weak anomaly in $\Delta n_{bc}$ near $T_{c1}$ is not reduced further by the application of field up to 20 kV/cm. Because the variation in $\Delta n_{bc}$ is related to the polarization changes, the data in Fig. 3 indicate that the ferroelectric phase-transition temperature does not increase linearly with the field. This result does not agree with the data of $\varepsilon'_a(T)$, where $dT_{c2}/dE \approx 0.9$ K/(kV/cm). It can be considered that the shift in the temperature of $\varepsilon'_a(T)$ maximum with electric field does not reflect directly change in ferroelectric transition temperature.

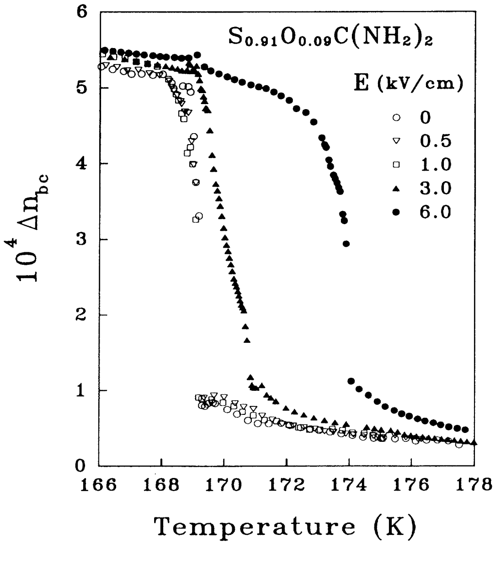

FIG 3. The temperature dependence of $\Delta n_{bc}$ near $T_c$ measured with different electric fields.

For mixed crystals, it can be conjectured that the ferroelectric domain walls are strongly pinned even under electric field. The domain walls may be the residual discommensurations,[15] which are not annihilated during the cooling process by defect pinning. These discommensurations are thought to favor a modulated structure through the interaction between them. The ferroelectric transition cannot be so affected by the field even though the dielectric-constant measurement shows some field-dependent changes for the field less than 1 kV/cm. The field dependence may originate from the superposition of different dielectric responses which will be discussed later.

If the bias field is increased, the pinning effect would be reduced, since the discommensurations can overcome the pinning potential. Some of the unstable discommensurations can move under the field and eventually will annihilate in pairs. The result of Fig. 3 with $E=6$ kV/cm is the case where most of the pinning potentials are overcome. The competition under electric field between the ferroelectric and $I$ phase results in the shift of the ferroelectric transition to higher temperature. Te data with $E=3$ kV/cm in Fig. 3 are likely to show an intermediate case. Only parts of discommensurations can overcome the pinning potential with the fields and a gradual transition occurs over a temperature range $T_{c1} < T < T_{c2}$. Both the ferroelectric and $I$ phases would coexist in this temperature range. Regions of ferroelectric state will increase with electric field at the expense of the $I$ regions.

However, the nature of the dielectric anomalies around $T_{c1}$ and $T_{c2}$ is not clear yet. Compared with $\Delta n_{bc}$, the $\varepsilon'_a(T)$ has two distinct maxima with $E=3$ kV/cm, while $\Delta n_{bc}$ shows a gradual change. For $E=6$ kV/cm, the peak value of $\varepsilon_a{}'$ at $T_{c1}$ is larger than that at $T_{c2}$, while the major change in $\Delta n_{bc}$ occurs around $T_{c2}$. Moreover, the dielectric loss ($\varepsilon''_a$) shown in Fig. 4 does not show any clear evidence for the phase transition near $T_{c2}$. The change of $\varepsilon''_a$ at $T_{c2}$ is very small and undistinguishable even under $E=6$ kV/cm. On the other hand, the $\varepsilon''_a$ shows a distinct change at $T_{c1}$ for all the electric field applied and decreases with the field below $T_{c1}$. These facts indicate that there exist different kinds of dielectric responses around $T_{c1}$ and $T_{c2}$. The large value of $\varepsilon''_a$ below $T_{c1}$ may be due to the relaxational motion of strongly pinned domain walls in the ferroelectric phase. The number of walls will decrease with increasing the electric field, which may result in the decrease of $\varepsilon''_a$. As the temperature is increased, nucleation of discommensurations would begin in the ferroelectric regions of the

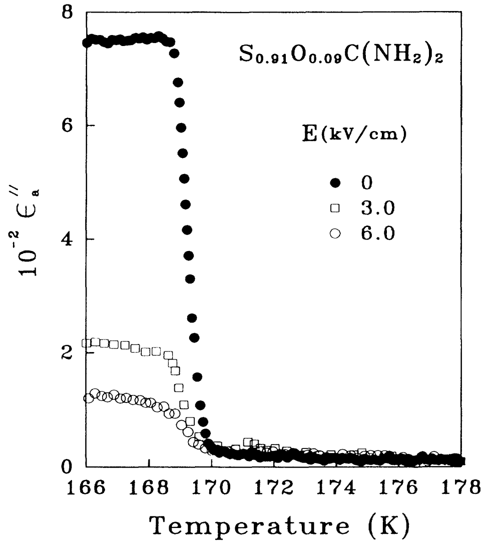

FIG. 4. The temperature dependence of $\varepsilon_a''$ near $T_c$ measured with different electric fields.

coexisting state. The dielectric constant peak at $T_{c2}$ may be related to the nucleation and fluctuation of the discommensurations (or ferroelectric domains on cooling). For $E=6$ kV/cm, most parts of the crystal are considered to be ferroelectric below $T_{c2}$. But, in the region $T_{c1} < T < T_{c2}$, a short-range ordering of the modulate structure around defects can be expected.

In summary, the field effects on the ferroelectric phase transition of urea-doped thiourea, $S_{0.91}O_{0.09}C(NH_2)_2$, have been investigated by measuring the complex dielectric constant ($\varepsilon_a'$ and $\varepsilon_a''$) and the LB $\Delta n_{bc}$. For the mixed crystal, the intermediate *C* phases are completely suppressed by the urea impurities. Splitting of phase transition, presumably related to the impurity pinning effect, is observed under electric field. The linear field dependence of the temperature $T_{c2}$, where the $\varepsilon_a'$ maximum locates, is found not to be related directly to the shift of ferroelectric phase transition. There seem to exist different kinds of dielectric responses near the $T_{c1}$ and $T_{c2}$, although we cannot address the origins clearly. Relaxational motion of the pinned domain walls, nucleation and fluctuation of discommensurations are discussed for the possible origins. The field-induced phase between the $T_{c1}$ and $T_{c2}$ is attributed to the coexistent phase of ferroelectric and *I* phases due to the defect pinning effect. Otherwise, the phase should be a homogeneous ferroelectric phase.

## ACKNOWLEDGMENTS

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Science Research Center (SRC) of Excellence Program. The authors would like to thank Professor Insuk Yu for his comments.

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