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Phase transition in triglycine sulfate crystals by ¹H and ¹³C nuclear magnetic resonance in the rotating frame

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HIGHLIGHTS

• The ferroelectric phase transition in triglycine sulfate ((NH₂CH₂COOH)₃·H₂SO₄, TGS)) crystals.

• The spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, of ¹H and ¹³C.

• The ferroelectric phase transition of TGS by ordering of the carboxyl groups.

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ABSTRACT

The ferroelectric phase transition in triglycine sulfate ($(NH_2CH_2COOH)_3 \cdot H_2SO_4$, TGS)) crystals, occurring at T_C of 322 K, was studied using ¹H and ¹³C CP/MAS NMR. From the spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, of ¹H and ¹³C, we found that the slopes of the $T_{1\rho}$ versus temperature curve changed near T_C . In addition, the change of intensities for the protons and carbons NMR signals in the ferroelectric and the paraelectric phases led to the noticeable changes in the environments of proton and carbon in the carboxyl groups. The carboxyl ordering was the dominant factor driving the phase transition. Our study of the ¹H and ¹³C spectra showed that the ferroelectric phase transition of TGS is of the order–disorder type due to ordering of the carboxyl groups.

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1. Introduction

Numerous experimental studies have investigated the relaxation behavior of ferroelectric crystals of triglycine sulfate $[(NH_2CH_2-COOH)_3 \cdot H_2SO_4; TGS]$ [1,2]. Nonlinearity of real ferroelectric crystals in ac electric fields has been observed in various studies [3–6]. The nonlinear properties of ferroelectric crystals remain poorly understood, and constitute a priority problem in ferroelectric physics [7]. The electrical properties and domain structures of ferroelectric TGS crystals have been discussed in recent publications [8–13]. TGS is a ferroelectric material that shows second-order phase transitions, with a Curie point at around room temperature [14]; the Curie temperature is 322 K (= T_C). The ferroelectric phase transition in TGS crystals has been extensively investigated, as it is a model example of a continuous second-order phase transition.

Blinc et al. [15] used nuclear magnetic pulsed double resonance in the rotating frame to study changes in the ¹⁴N quadrupole interactions in the ferroelectric and paraelectric phases of a TGS crystal. The most significant effects of the ferroelectric transition were a large change in the time-averaged value of the C-N bond direction of glycine I, and the onset of the chemical inequivalence of glycines II and III due to ordering of the protons in the short $O-H \cdots O$ bond. The cited authors concluded that the phase transition was of the order-disorder type, on the basis of their pulsed proton-nitrogen double resonance study [15]. The temperature dependence of the proton spin-lattice relaxation time, T_1 , in TGS was investigated near the transition temperature by Blinc et al. [16] and Tsujimi et al. [17]. Despite the important role of these materials in various applications, unresolved problems remain regarding the mechanism of the ferroelectric phase transition. Although ¹H spin-lattice relaxation time *T*₁ and ¹⁴N NMR spectrum investigations of TGS in the laboratory frame have been conducted over the last years, the protons and carbons in the ferroelectric and paraelectric phases have not been discussed. For instance, there is a lack of information obtained from dynamic measurements, such as measurements of the spin-lattice relaxation time $T_{1\rho}$ in a rotating frame for each proton and carbon.

To investigate the influence of structural changes on the phase transition properties of TGS, we studied the nature of each proton





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and carbon. Specifically, to better elucidate the nature of the ferroelectric phase transition in these crystals, and, in particular, to obtain a better understanding of the internal molecular motion in the ferroelectric and paraelectric phases, we measured the temperature dependence of the nuclear magnetic resonance (NMR) spectrum and the nuclear spin–lattice relaxation times in the rotating frame $T_{1\rho}$ for ¹H and ¹³C in TGS. Based on these results, we will discuss the roles for the each proton and carbon.

2. Crystal structure

TGS crystals with the phase transition temperature of 322 K are monoclinic in ferroelectric phase, and belong in the high-temperature paraelectric phase of the centro-symmetrical space group $P2_1/$ m. Below the Curie point, the mirror plane disappears and the space group is P2₁. The ferroelectric transition is of second-order, and the spontaneous polarization is parallel to the monoclinic baxis. The crystal structure of TGS projected along the c-axis is shown in Fig. 1 [18]. The lattice constants in ferroelectric phase are a = 9.1666 Å, b = 12.6436 Å, c = 5.7339 Å, and $\beta = 105.5^{\circ}$ [18,19]. There are two formula units per unit cell: $(NH_3^+CH_2COO^-)$ and $(NH_2CH_2COOH)_2 H_2SO_4$ [20]. In the ferroelectric phase, the two monoprotonated glycine groups I and III (NH₂₋ CH₂COOH and NH₃⁺CH₂COO⁻, hereinafter designated G(I) and G(III)) are completely planar, whereas the zwitterions (NH₃⁺CH₂COO⁻, hereinafter designated G(II)) are only partially planar [15,21]. The nitrogen atoms form N–H···O hydrogen bonds of the usual strength, whereas the strong $O-H\cdots O$ hydrogen bond incorporating the oxygen atom of the carboxyl group of the zwitterion glycine has a distance of 2.43 Å [21]. The bond distances and angles in G(I) change only slightly with temperature, whereas the variations in G(II) and G(III) are significant [18].

3. Experimental method

TGS single crystals were grown at room temperature by slowly evaporating an aqueous solution containing NH₂CH₂COOH and H₂SO₄ in the stoichometric ratio of 3:1. The chemical formula of TGS is (NH₃⁺CH₂COO⁻) and (NH₂CH₂COOH)₂·H₂SO₄. The resulting single crystals were transparent and colorless with dimensions of $10 \times 10 \times 5 \text{ mm}^3$.

Solid-state NMR experiments were performed using a Bruker DSX 400 FT NMR spectrometer at the Korea Basic Science Institute.

Cross-polarization, magic angle spinning (CP/MAS) ¹H and ¹³C NMR experiments were performed at a Larmor frequency of 400.12 MHz and 100.61 MHz, respectively. The samples were placed in the 4 mm CP/MAS probe as powders. The magic angle spinning rate was set at 14 kHz and 4–6 kHz for ¹H and ¹³C CP/MAS, respectively, to minimize spinning sideband overlap. The $\pi/2$ pulse time for ¹H and ¹³C was 10 µs and 16.8 µs, respectively, corresponding to a spin-locking field strength of 27.77 kHz and 46.66 kHz. The ¹H and ¹³C $T_{1\rho}$ measurements were performed by applying ¹H and ¹³C spin-locking pulses after the CP preparation period.

4. Experimental results and discussion

Structural analysis of the protons in TGS was carried out by a solid state NMR method. Fig. 2a shows the ¹H MAS NMR spectrum of a TGS single crystal at room temperature. The NMR spectrum consists of three peaks, at chemical shift of δ = 7.60, 15.15, and 18.22 ppm. The spinning sidebands are marked with asterisks. The signal at chemical shift of 7.60 ppm is assigned to the ammonium hydrogen, methylene proton, and amine hydrogen. The signals at chemical shifts of 15.15 ppm and 18.22 ppm are assigned to the carboxyl hydrogen and hydrogen sulfate, respectively.

The intensities in the each proton signals as a function of temperature for TGS are shown in Fig. 2b. As the temperature is increased, the intensity of the signal due to the ammonium hydrogen, methylene proton, and amine hydrogen (labeled as 1, 2, and 3) is near constant. The intensities of the signals due to the carboxyl hydrogen (labeled as 4) and hydrogen sulfate (labeled as 5) are abruptly decrease with temperature, whereas those of the carboxyl hydrogen and hydrogen sulfate is nearly constant above T_c , indicating that the carboxyl hydrogen and hydrogen sulfate play an important role in the phase transition. Usually, the dynamic ordering of hydrogen occurs in one of the hydrogen bonds as the material transforms into the ferroelectric phase [22].

The spin–lattice relaxation times in the rotating frame, $T_{1\rho}$, were taken at several temperatures for the each proton in TGS. The nuclear magnetization recovery traces obtained for all protons were described by the following single exponential function [23]:

$$M(t) = M_o \exp(-t/T_{1\rho}) \tag{1}$$



Fig. 1. The crystal structure of ferroelectric (NH₂CH₂COOH)₃·H₂SO₄ projected along the *c*-axis. Dashed lines show the hydrogen bonds [18].



Fig. 2. (a) Solid state ¹H MAS NMR spectrum for TGS at room temperature and (b) the intensity variations of each proton in TGS as a function of temperature (1, 2, and 3: ammonium hydrogen, methylene proton, and amine hydrogen; 4: carboxyl hydrogen; 5: hydrogen sulfate).

where M(t) is the magnetization at time t, and M_o is the total nuclear magnetization of ¹H at thermal equilibrium. The recovery traces are shown in Fig. 3 for delay times ranging from 0.001 ms to 300 ms at room temperature. The recovery traces showed a single exponential decay at all temperatures. The slopes of the recovery traces are different at each temperature. The ¹H spin–lattice relaxation time in the rotating frame is shown in Fig. 4 as a function of inverse temperature. While the proton T_{1o} data show changes in slope at T_c , there



Fig. 3. The saturation recovery traces of ¹H in TGS as a function of delay time at room temperature.

is no evidence of an anomalous decrease in $T_{1\rho}$ near T_c . The relaxation time increased as the temperature was increased above the temperature at which a minimum was observed (i.e., 190 K). The minimum in $T_{1\rho}$ at 190 K indicates that distinct molecular motion of protons is present. The form of the proton $T_{1\rho}$ versus inverse temperature curve indicates that the relaxation process occurs via molecular motion. The $T_{1\rho}$ values can be related to the rotational correlation time, τ_c which corresponds to the length of time that a molecule remains in a given state before undergoing reorientation. Thus, τ_c is a direct measure of the rate of rotational motion. The experimental value of $T_{1\rho}$ can be expressed in terms of the isotropic correlation time for molecular motion using the Bloembergen-Purcell-Pound (BPP) function [24]. According to the BPP theory, the $T_{1\rho}$ value for a spin–lattice interaction in the case of random motion is given by

$$(nT_{1\rho}^{-1}) = 0.05(\gamma_H\gamma_C h/r_{H-C}^3)^2 [4A + B + 3C + 6D + 6E]$$
(2)
where

$$A = \tau_C / [1 + \omega_1^2 \tau_C^2]$$

$$B = \tau_C / [1 + (\omega_H - \omega_C)^2 \tau_C^2]$$

$$C = \tau_C / [1 + \omega_H^2 \tau C^2)$$

$$D = \tau_C / [1 + (\omega_H + \omega_C)^2 \tau_C^2]$$

$$E = \tau_C / [1 + \omega_H^2 \tau_C^2]$$

Here, γ_H and γ_C are the gyromagnetic ratio for the ¹H and ¹³C nuclei, respectively, n is the number of directly bound protons, r is the H–C internuclear distance, $\hbar = h/2\pi$ (where *h* is Planck's constant), ω_H and ω_C are the Larmor frequencies of ¹H and ¹³C, respectively, and ω_1 is the spin-lock field. The analysis of our data was carried out assuming that $T_{1\rho}$ would show a minimum when $\omega_1 \tau_c$ = 1, and that the BPP relation between $T_{1\rho}$ and the characteristic frequency of motion ω_1 could be applied. Since the $T_{1\rho}$ curves were found to exhibit minima, it was possible to determine the coefficient in the BPP formula. Having determined this coefficient, we were then able to calculate the parameter τ_{C} as a function of temperature. The temperature dependence of $\tau_{\rm C}$ followed a simple Arrhenius expression, $\tau_{C} = \tau_{o} \exp((-E_{a}/RT))$, where τ_{o} is the preexponential factor, T is the temperature, R is the gas constant, and E_a is the activation energy. Thus, the slope of the straight-line portion of the semilog plot could be used to determine the activation energy, E_a . The activation energy for the molecular motion can



Fig. 4. The ¹H spin-lattice relaxation time, *T*₁*ρ*, in the rotating frame for the TGS as a function of inverse temperature.

be obtained from the log τ_c versus 1000/T curve, as shown in Fig. 5. The pre-exponential factors for each proton were as shown in Table 1. Below and above T_c , the activation energies were obtained, and observed that the change of E_a for the hydrogen sulfate (5) was larger than that of other protons (1, 2, 3, and 4).

Structural analysis of the carbons in TGS was carried out using ¹³C NMR spectroscopy. Fig. 6a shows the solid-state ¹³C CP/MAS NMR spectrum. The ¹³C NMR spectrum for TGS shows four signals, at chemical shifts of δ = 41.04, 42.59, 170.43, and 173.97 ppm. The spinning sidebands are marked with asterisks. The signals at chemical shifts of δ = 41.04 ppm and δ = 42.59 ppm represent the methylene carbons in (NH₃⁺CH₂COO⁻) and (NH₂CH₂COOH)₂·H₂SO₄, respectively, while the signals at δ = 170.43 ppm and δ = 173.97 ppm represent the carboxylate in (NH₃⁺CH₂COO⁻) and the carboxylic acid in (NH₂CH₂COOH)₂·H₂SO₄, respectively.

The variations in the carbon peak intensities as a function of temperature for a TGS are shown in Fig. 6b. As the temperature is increased, the intensities of the signals due to the methylene carbons (NH₃⁺CH₂COO⁻ and NH₂CH₂COOH) remain constant, whereas the intensities of the signals due to the carboxyl groups in NH₃⁺CH₂COO⁻ and NH₂CH₂COOH decrease near T_G, indicating that the carboxyl groups play an important role in the phase transition. Based on these results, we attribute the temperature-dependent decrease in the intensity of the carboxyl group signals to the ordering of the carboxyl groups. Prompted by the result reported in the literature [22] that dynamic ordering of hydrogen occurs in one of the hydrogen bonds as the material goes into the ferroelectric phase, we propose that the decrease of the intensity of the signal from carbons with temperature is related to the ordering of such protons.



Fig. 5. Arrhenius plot of the natural logarithm of the correlation times for proton as a function of the inverse temperature.



Fig. 6. (a) Solid state ¹³C CP/MAS NMR spectrum for TGS at room temperature and (b) the intensity variations of each carbon in TGS as a function of temperature (1 and 2: methylene carbons; 3 and 4: carboxyl groups).

The spin-lattice relaxation times in the rotating frame, $T_{1\rho}$, were taken for each carbon in the TGS at several temperatures, with variable spin locks on the carbon channel following cross polarization. The ¹³C magnetization was generated by cross-polarization, after spin locking of the protons. The proton field was then turned off for a variable time *t*, while the ¹³C rf field remained on. Finally, the ¹³C free induction decay was observed under high power proton decoupling, and was subsequently Fourier transformed. Values of $T_{1\rho}$ could be selectively obtained by the Fourier transformation of the FID, following the end of spin locking and repetition of the experiment with variations in the time *t*. All of

Table 1

The pre-exponential factor τ_o and activation energy E_a for ¹H below and above T_C of ammonium hydrogen (1), methylene proton (2), amine hydrogen (3), carboxyl hydrogen (4), and hydrogen sulfate (5) in TGS.

Label for protons	τ _o Present work ^a	<i>E_a</i> (kJ/mol) Present work ^a	<i>E_a</i> (kJ/mol) Blinc et al. ^b [16]	<i>E_a</i> (kJ/mol) Tsujimi et al. ^b [17]	E _a (kJ/mol) Brosowski et al. ^b [25]
$T < T_C$					
1,2, and 3	$9.00 imes 10^{-12}$	19.19 ± 1.49	22.18	20.25	24.11
4	$1.45 imes 10^{-11}$	18.30 ± 1.49			
5	1.62×10^{-12}	22.21 ± 1.60			
$T > T_C$					
1,2, and 3	1.49×10^{-10}	11.73 ± 1.37	22.18	17.36	21.22
4	$8.78\times\mathbf{10^{-11}}$	12.64 ± 0.88			
5	$\textbf{4.48}\times \textbf{10}^{-11}$	13.47 ± 0.76			

^a The data obtained by ¹H $T_{1\rho}$.

^b The data obtained by ¹H T_1 .



Fig. 7. Temperature dependences of the ¹³C spin–lattice relaxation time, $T_{1\rho}$, in the rotating frame for the TGS.

the traces obtained for the carbons were described by a single exponential function of Eq. (1). The $T_{1\rho}$ values for methylene and the carboxyl groups are shown in Fig. 7. In the case of the carboxyl groups (labeled as 3 and 4), the ¹³C $T_{1\rho}$ increased rapidly with increasing temperature, whereas the ¹³C $T_{1\rho}$ for the methylene carbons (labeled as 1 and 2) increased very slowly with increases in temperature.

5. Conclusion

To further elucidate the nature of the microscopic structural changes that occur on going from the ferroelectric to the paraelectric phase, we measured the NMR spectra of protons and carbons in TGS crystals. In addition, NMR studies of the ¹H and ¹³C spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, were discussed, and it was found that the slope of the $T_{1\rho}$ versus temperature curve changed near T_C . From these results, the NMR spectrum was found to be more sensitive than the relaxation time to the phase transition in this crystal. The slopes for $T_{1\rho}$ of the each proton show change near $T_{\rm C}$ and the distinct molecular motions of protons were present. According to Blinc et al. [16], the transition from the paraelectric to the ferroelectric phase at 320 K was indeed accompanied by an anomalous decrease in the proton T_1 , indicating a significant decrease of the proton motion in the ferroelectric phase. From this result, E_a was shown to have same values in both phases as shown in Table 1. Brosowski et al. [25] have reported a nonmonotonic anomaly of proton T_1 near T_c , whereas the Tsujmi et al. [17] did not observe the anomalous behavior in T_1 . However, the E_a of this hindered rotation appeared to have similar value. The E_a obtained from $T_{1\rho}$ here were consistent with those obtained from T₁ reported by Blinc et al. [16], Tsujimi et al. [17], and Brosowski et al. [25], as shown in Table 1; the E_a in $T < T_C$ is much larger than those in $T > T_c$. The values of T_1 and E_a previously reported were not distinguishable in each proton sites. However, we were able to resolve ¹H MAS NMR spectrum into the ammonium hydrogen, methylene proton, amine hydrogen, carboxyl hydrogen, and hydrogen sulfate, respectively. Additionally, methylene carbons and carboxyl groups from ¹³C CP/MAS NMR spectrum were also distinguished. The molecular motions of the carboxyl groups in the ferroelectric phase were very large, whereas those of the methylene carbons were not large. Changes in ¹³C $T_{1\rho}$ associated with the carboxyl groups were observed at the transition from the ferroelectric to the paraelectric phase. The changes in the environments of proton and carbon in the carboxyl groups in the ferroelectric and the paraelectric phases led to the noticeable change in the proton and carbon magnetic resonance spectra, respectively. The intensities of the signals due to the carboxyl groups decreased with increasing temperature, consistent with ordering of the carboxyl groups. Indeed, carboxyl ordering was the dominant factor driving the phase transition. The ferroelectric phase transition observed in the present work was of order-disorder type in terms of the proton and carbon in the carboxyl groups as determined by ¹H and ¹³C NMR. These results shed new light on phase transitions involving the ¹H and ¹³C in TGS.

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