



Molecular Dynamics in Paraelectric Phase of KH_2PO_4 Crystals Studied by Single Crystal NMR and MAS NMR

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Abstract The temperature dependences of the NMR spectrum and the spin-lattice relaxation times in KH_2PO_4 were investigated via single-crystal NMR and MAS NMR. The stretched-exponential relaxation that occurred because of the distribution of correlation times was indicative of the degree of the distribution of the double-well potential on the hydrogen bond. The behaviors responsible for the strong temperature dependences of the ^1H and ^{31}P spin-lattice relaxation times in the rotating frame $T_{1\rho}$ in KH_2PO_4 are likely related to the reorientational motion of the hydrogen-bond geometry and the PO_4 tetrahedral distortion.

Keywords NMR, CP/MAS NMR, Crystal growth, Phase transition, Ferroelectrics

Introduction

Potassium dihydrogen phosphate (KH_2PO_4) is among the most widely used crystals in nonlinear optics and the electro-optics industry owing to its unique properties such as a wide region of optical transparency, ferroelectric and piezoelectric stability against high-power laser light, and relatively high nonlinear efficiency^{1,2}. At $T_C=122$ K, KH_2PO_4 crystals undergo a ferroelectric phase transition from a tetragonal noncentrosymmetric phase (42m), at temperatures above T_C , to an orthorhombic polar

phase (mm2), at temperatures below T_C .^{3,4} The hydrogen-bonded KH_2PO_4 system has been a popular subject of scientific interest and debate for the structure dynamics aspect of its ferroelectric phase transition mechanism. The elements of the crystal structure that interest us are the phosphate groups, $(\text{PO}_4)^{3-}$, and the hydrogen bond protons; the potassium atoms merely have fixed positions in the crystal and serve only to hold it together. A phosphate group consists of a phosphorus atom tetrahedrally surrounded by four oxygens⁵. The structure of the crystal in paraelectric phase is shown in Fig. 1.

Hydrogen motion in KH_2PO_4 has been reported by scientists investigating the rotating frame protons' spin-lattice relaxation measurement at room temperature to about 373 K⁶. Much less is understood, however, about the structural, chemical, and physical property changes that occur in KH_2PO_4 upon heating it from room temperature to its melting point. Thermal events observed around $T_P\sim 458$ K have been attributed by Grunberg et al.⁷ and Botez et al.⁸ to a polymorphic phase transition that occurs because of an intermediate temperature KH_2PO_4 modification, while Lee⁹ and Ortiz et al.¹⁰ have claimed that the behavior at T_P is attributable to chemical changes such as dehydration and the onset of partial polymerization of tetragonal KH_2PO_4 phase at room temperature.

Measurements of the spin-lattice relaxation time in

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the rotating frame $T_{1\rho}$ by magic angle spinning nuclear magnetic resonance (MAS NMR) are able to probe the molecular motion in kilohertz, whereas the spin-lattice relaxation time in the laboratory frame T_1 by single-crystal NMR only reflect motion in the megahertz range. To the best of our knowledge, the spin-lattice relaxation times in the laboratory frame T_1 and in the rotating frame $T_{1\rho}$ of the paraelectric phase of KH_2PO_4 have not been published previously. In this study, the paraelectric phase of KH_2PO_4 was studied by determining the NMR relaxation times. In particular, we investigated the molecular motion in the paraelectric phase by measuring the temperature dependences of the T_1 and $T_{1\rho}$ for ^1H and ^{31}P ions. In this regard, we show that there exists an opportunity to study the effects of the microscopic structure of the hydrogen bond geometry and PO_4 tetrahedral distortion in the KH_2PO_4 .

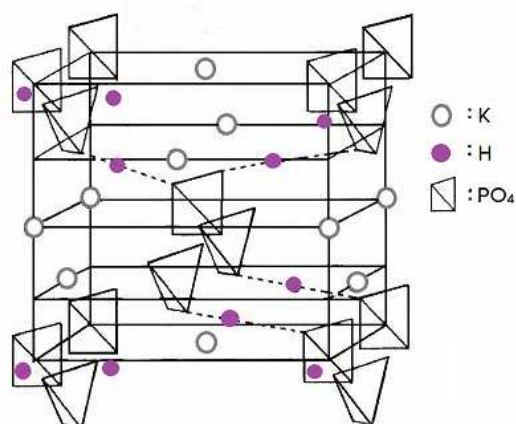


Figure 1. The crystal structure of KH_2PO_4 in the paraelectric phase.

Experimental Methods

The KH_2PO_4 single crystals, which exist as colorless hexagonal shapes, were grown by using the slow evaporation method from an aqueous solution. The NMR signals of the ^1H and ^{31}P nuclei in the KH_2PO_4 single crystals were measured with the Bruker 200 FT NMR and 400 FT NMR spectrometers at the Korea Basic Science Institute. The static magnetic

fields were 4.7 T and 9.4 T, respectively, and the central radio frequencies were set at $\omega_0/2\pi = 200$ MHz for the ^1H nucleus and $\omega_0/2\pi = 161.98$ MHz for the ^{31}P nucleus. The NMR spectrum and the spin-lattice relaxation time T_1 in the laboratory frame was obtained with the magnetic field applied parallel to the c -axis of the crystal. The ^1H and ^{31}P T_1 measurements were performed using $(\pi/2)_{\text{sat}}-t-\pi/2$ pulse sequences. The nuclear magnetizations $M(t)$ of the ^1H and ^{31}P nuclei at time t after the $(\pi/2)_{\text{sat}}$ pulses were determined from the saturation recovery sequence following each pulse. The widths of the $\pi/2$ pulses were 2.6 μs for ^1H and 2.5 μs for ^{31}P .

To obtain the spin-lattice relaxation times $T_{1\rho}$ in the rotating frame, solid state NMR experiments were performed using a Bruker 400 MHz NMR spectrometer. ^1H and ^{31}P MAS NMR experiments were performed at the Larmor frequency of $\omega_0/2\pi = 400$ MHz and $\omega_0/2\pi = 161.98$ MHz, respectively. Powder samples were placed in the 4 mm CP/MAS probe, and the MAS rate was set to 10 kHz for ^1H and ^{31}P MAS in order to minimize the spinning sideband overlap. The width of the $\pi/2$ pulse for ^1H and ^{31}P were 5 μs and 2.5 μs . The spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, was measured by applying spin-locking pulses of 50 kHz for ^1H and 100 kHz for ^{31}P , respectively. The NMR measurements were obtained in the temperature

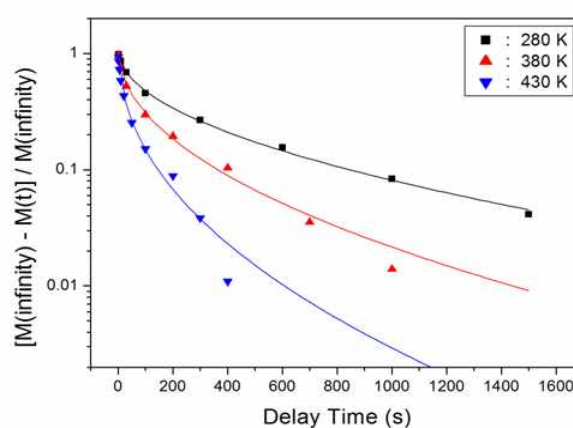


Figure 2. ^1H nuclear magnetization recovery as a function of delay time at 280 K, 380 K, and 430 K in KH_2PO_4 single crystals (the solid lines show fits to the stretched-exponential form, $M(t) = M_0[1 - \exp(-t/T_1)^{1-n}]$)

range 180–430 K. Unfortunately, the relaxation times could not be determined above 430 K because the NMR spectrometer did not have adequate temperature controlling system at high temperature. The sample temperatures were maintained at constant values by controlling the helium gas flow and the heater current.

Experimental Results and Analysis

The ^1H magnetizations for this crystal in the laboratory frame were measured over a wide temperature range. The recovery traces of ^1H at three specific temperatures are shown in Fig. 2. The measured magnetization recovery could not be fitted to a single exponential, but it was well fitted to the stretched exponential function¹¹,

$$[M(\infty) - M(t)]/M(\infty) = \exp(-t/T_1)^{1-n} \quad (1)$$

According to the NMR theory, stretched-exponential relaxation occurs due to the distribution of correlation times; in the paraelectric phase KH_2PO_4 , the exponent n for the stretched-exponential is also indicative of the degree of the distribution of the double-well potential on the hydrogen bond. The

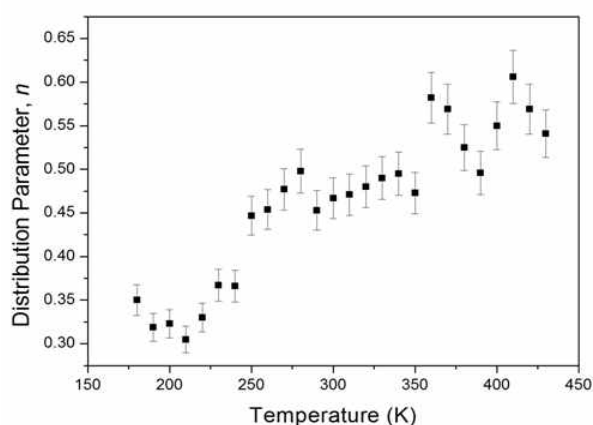


Figure 3. Temperature dependence of the stretched-exponential fit obtained from ^1H NMR spin-lattice relaxation measurements in KH_2PO_4 single crystals.

exponent n exhibited a significant variation with temperature up to 210 K, as displayed in Fig. 3. The temperature dependence of the exponent n for the stretched-exponential fit, which was defined as an order parameter for the proton double-well distribution in the KH_2PO_4 work, is also shown in Fig. 3.

The ^1H spin-lattice relaxation times in the laboratory frame, T_1 , of the KH_2PO_4 crystals were obtained with the saturation recovery method at $\omega_0/2\pi = 200$ MHz, as shown in Fig. 4. The relaxation time, T_1 , was determined directly from the slope of the plot of $\log [M(\infty) - M(t)]/M(\infty)$ versus time, t , described by Eq. (1). In addition, structural analysis of the protons in KH_2PO_4 was carried out by a solid state NMR method at $\omega_0/2\pi = 400$ MHz. We also obtained the ^1H MAS NMR spectrum of a KH_2PO_4 as a function of temperature and determined that it consists of one peak at a chemical shift of $\delta = 14.73$ ppm, and that this signal is assigned to the hydrogen-bond protons. The ^1H spin-lattice relaxation time in the rotating frame $T_{1\rho}$ at all temperatures is described by the following single exponential function: $M(t) = M(\infty) \exp(-t/T_{1\rho})$ ¹². The spin-lattice relaxation time in the rotating frame is shown as a function of temperature in the inset in Fig. 4. T_1 is longer than $T_{1\rho}$, indicating

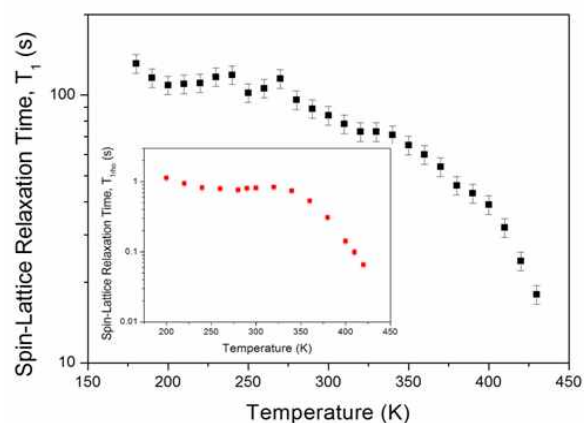


Figure 4. Temperature dependence of the spin-lattice relaxation time in the laboratory frame T_1 for ^1H in a KH_2PO_4 single crystal (inset : temperature dependence of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for ^1H in a KH_2PO_4).

a monotonic decrease, whereas $T_{1\rho}$ abruptly decreases with increasing temperature.

The ^{31}P nuclei of spin $I = 1/2$ in KH_2PO_4 crystals give rise to a single resonance line at $\omega_0/2\pi = 161.98$ MHz. The saturation recovery traces for ^{31}P can be represented by a single exponential form at all investigated temperatures. Fig. 5 shows delay times ranging from 100 s to 4000 s at 300 K. The spin-lattice relaxation times in the laboratory frame T_1 for ^{31}P are shown as a function of temperature in Fig. 6. Further, the magnetization recovery trace needed to obtain the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ was obtained by a single

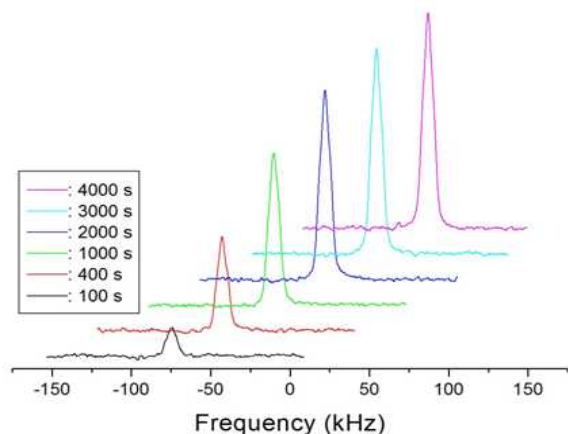


Figure 5. Saturation recovery traces for ^{31}P nucleus as a function of delay time at room temperature in KH_2PO_4 single crystals.

exponential function, $M(t) = M(\infty) \exp(-Wt)$, and $T_{1\rho}$ was determined as $1/W$. The measured values of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ is shown in the inset in Fig. 6. T_1 slowly decreases with increasing temperature, whereas $T_{1\rho}$ decreases abruptly. This sharp decrease in $T_{1\rho}$ can be ascribed to the onset of slow translational diffusion of the ^{31}P nucleus.

Discussion and Conclusion

We have examined the temperature dependences of the spin-lattice relaxation times in laboratory and

rotating frames for KH_2PO_4 using an FT NMR spectrometer. The molecular dynamics of KH_2PO_4 were investigated by examining the spin-lattice relaxation times T_1 and $T_{1\rho}$ in the paraelectric phase. Although the spin-lattice relaxation time T_1 of ^1H and ^{31}P ions in high temperature change slowly, the spin-lattice relaxation time $T_{1\rho}$ of ^1H and ^{31}P decreases abruptly. In particular, the observed changes in the temperature dependence of $T_{1\rho}$ at high temperatures are related to variations in the symmetry of the environments of H^+ and P^{5+} . The behavior that gives rise to the strong $T_{1\rho}$ temperature dependence for ^1H and ^{31}P in KH_2PO_4 at high

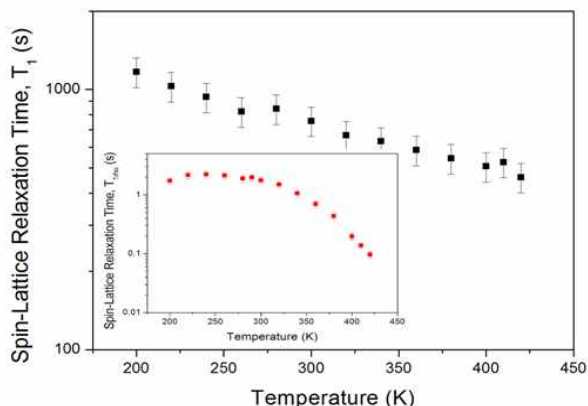


Figure 6. Temperature dependence of the spin-lattice relaxation time in the laboratory frame T_1 for ^{31}P in a KH_2PO_4 single crystal (inset: temperature dependence of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ for ^{31}P in a KH_2PO_4).

temperatures is likely to be related to the orientations of the tetrahedral PO_4 groups and the hydrogen-bond protons in the kilohertz range. The molecular motion in the paraelectric phase of KH_2PO_4 is not only dominated by proton order-disorder but also is coupled to other order parameters, such as the distribution of the PO_4 tetrahedra. The molecular motions in the paraelectric phase are affected more by $T_{1\rho}$ in the kilohertz range than by T_1 in the megahertz range.

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