

Phase-transition-like phenomenon of $\text{NH}_4\text{H}_2\text{PO}_4$ observed using MAS NMR and static NMR near characteristic temperature

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Abstract We used Fourier-transform nuclear magnetic resonance (NMR) spectroscopy to investigate the temperature dependences of the chemical shift and resonance frequency observed with magic-angle spinning NMR and static NMR, respectively, to confirm a high-temperature behavior of $\text{NH}_4\text{H}_2\text{PO}_4$. The hydrogen bonds in both O–H–O between two PO_4 groups and N–H–O between NH_4 and PO_4 were distinguished, and the changes occurring in the chemical shift and resonance frequency near the characteristic temperature T_p are related to changes in the atomic positions. The experimental results of thermogravimetric analysis conducted to interpret the high-temperature phenomena without the critical change around T_p are consistent with a phase-transition-like phenomenon at T_p .

Keywords $\text{NH}_4\text{H}_2\text{PO}_4$ · Chemical shift · Phase transition · MAS NMR · Nuclear magnetic resonance

Introduction

Several dihydrogen phosphate salts, MH_2PO_4 , are of technological interest because they exhibit ferroelectric ($M = \text{K}, \text{Rb}, \text{Cs}$) or antiferroelectric ($M = \text{NH}_4$) properties at low temperature [1–3]. MH_2PO_4 compounds have also

been suggested to be suitable for fuel-cell applications because they undergo a superionic phase transition at high temperatures [4–13]. $\text{NH}_4\text{H}_2\text{PO}_4$, a member of the KH_2PO_4 family, shows a high-temperature phase transformation at the characteristic temperature $T_p = 430 \text{ K}$ [14]. In addition, $\text{NH}_4\text{H}_2\text{PO}_4$ undergoes a paraelectric-to-antiferroelectric phase transition at $T_C = 148 \text{ K}$ [15]. In the paraelectric phase, the crystal is tetragonal with the space group $I42d$, whereas in the antiferroelectric phase, it is orthorhombic with the space group $P2_12_12_1$. The structure of this paraelectric phase is shown in Fig. 1 [16, 17]. Two types of hydrogen bonds linking PO_4 ions and NH_4 ions were reported; in $\text{NH}_4\text{H}_2\text{PO}_4$, hydrogen bonds exist in both O–H–O between two PO_4 groups and N–H–O between NH_4 and PO_4 ions [18–21].

The high-temperature behavior of $\text{NH}_4\text{H}_2\text{PO}_4$ has been investigated in several studies. However, there are many discrepancies in the high-temperature phase transition temperature T_p . Viswanath and Miller [22] found a sharp increase in the conductivity at 430 K and attributed it to a structural phase transition. They also confirmed this transition by infrared spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TG). Torijano et al. [23] observed using TG that, when heating $\text{NH}_4\text{H}_2\text{PO}_4$ powder above 430 K, a rapid mass loss occurs starting at approximately 463 K, which is attributed to the thermal dehydration of the sample. In addition, Park et al. [24] reported that the mechanisms of electrical conductivity in H-bonded crystals must include thermal dehydration as well as ionic transport, because it is known that many H-bonded crystals show surface instabilities such as thermal dehydration at high temperature. The study on the surface transformation of hydrogen-bonded crystals at high temperatures and topochemical nature was discussed by Lee [25]; the hydrogen-bonded crystals near temperature

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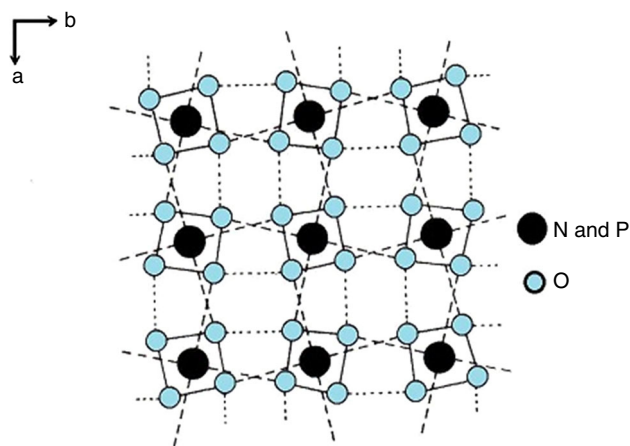


Fig. 1 Schematic structure of $\text{NH}_4\text{H}_2\text{PO}_4$ projected on the ab plane showing two types of hydrogen bonds. Dotted lines denote O–H–O bonds; broken lines represent N–H–O bonds

T_p were sensitive to changes in the conditions at the surface and seem to be due to an onset of thermal decomposition at the surface. On the other hand, Eichele and Wasylshen [1] conducted a ^{31}P nuclear magnetic resonance (NMR) study of powder and single-crystal $\text{NH}_4\text{H}_2\text{PO}_4$. Recently, NMR measurements have been used to investigate the molecular motions of the hydrogen bond in N–H–O between NH_4 and PO_4 , hydrogen bond in O–H–O between two PO_4 groups, and ^{31}P ions in PO_4 groups to confirm a high-temperature behavior of $\text{NH}_4\text{H}_2\text{PO}_4$ [7]. Although many researchers have studied these crystals both experimentally and theoretically, the mechanism of high-temperature phase transformation is still not completely understood.

In this study, the geometric structure of the hydrogen bond in N–H–O between NH_4 and PO_4 , hydrogen bond in O–H–O between two PO_4 groups, ^{31}P ions in PO_4 groups, and ^{14}N ions in NH_4 groups of $\text{NH}_4\text{H}_2\text{PO}_4$ was investigated by the chemical shift and resonance frequency by magic-angle spinning (MAS) NMR and static NMR. The mechanisms of phase transition were elucidated by measuring the temperature dependences of the chemical shift and resonance frequency for ^1H , ^{14}N , and ^{31}P ions by using Fourier-transform NMR spectroscopy. On the basis of the results, we discussed a phase-transition-like phenomenon at the characteristic temperature T_p .

Experimental

$\text{NH}_4\text{H}_2\text{PO}_4$ single crystals were grown by the slow evaporation of an aqueous solution. The single crystals obtained here had tetragonal shapes and were colorless.

TG was carried out under N_2 atmosphere on Du Pont 910 equipment. The samples were heated at a rate of $10\text{ }^\circ\text{C min}^{-1}$.

Solid-state NMR experiments in a rotating frame were performed using a Bruker 400 MHz NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The ^1H MAS NMR and ^{31}P MAS NMR experiments were performed at Larmor frequencies of $\omega_0/2\pi = 400.13$ and $\omega_0/2\pi = 161.98$ MHz, respectively. Powdered samples were placed in the 4-mm MAS probe. The MAS rate was set to 10 kHz for ^1H and ^{31}P MAS to minimize the spinning sideband overlap. The widths of the $\pi/2$ pulses for ^1H and ^{31}P were 5 and 25 μs , respectively.

In addition, the ^{14}N NMR spectra of the $\text{NH}_4\text{H}_2\text{PO}_4$ single crystals in the laboratory frame were measured using a Unity INOVA 600 NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. The static magnetic field was 14.1 T, and the Larmor frequency was set to $\omega_0/2\pi = 43.342$ MHz. The ^{14}N NMR experiments were performed using a solid-state echo sequence: $4.5\ \mu\text{s}-\tau$ (12 μs)– $4.5\ \mu\text{s}-\tau$ (12 μs). The NMR measurements were obtained in the temperature range of 180–440 K. Unfortunately, the chemical shift and resonance frequency could not be measured above 440 K because the NMR spectroscopy did not have adequate temperature control at high temperature. All the sample temperatures were maintained at constant values by controlling the helium gas flow and heater current, which yielded an accuracy of ± 0.5 K.

Results and discussion

TG was used to determine whether these high-temperature transformations are structural phase transitions or chemical reactions. Figure 2 shows the resulting curve of $\text{NH}_4\text{H}_2\text{PO}_4$ at heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The first occurrence of mass loss begins at approximately 430 K, accompanied by the escape of H_2O , as in the following chemical reaction reported by Lee [14]:

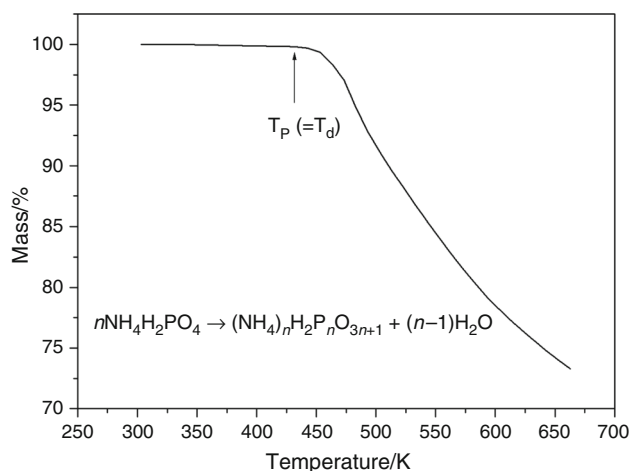


Fig. 2 Thermogravimetric analysis of $\text{NH}_4\text{H}_2\text{PO}_4$ crystal

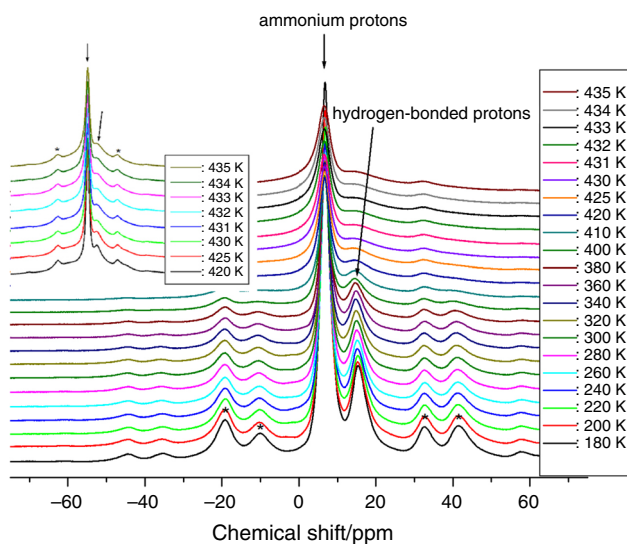


Fig. 3 In situ ^1H MAS NMR spectra of $\text{NH}_4\text{H}_2\text{PO}_4$ for different temperatures (Inset ^1H MAS NMR spectra in $\text{NH}_4\text{H}_2\text{PO}_4$ above 420 K)

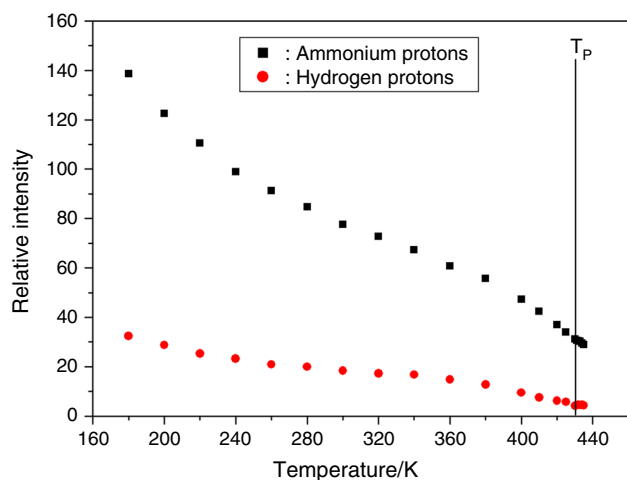
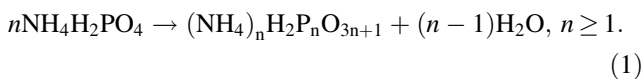


Fig. 4 Relative intensity of ^1H MAS NMR spectrum of $\text{NH}_4\text{H}_2\text{PO}_4$ as a function of temperature



This phenomenon is also consistent with the liquid-like behavior such as H_2O flow at the surface above T_p reported by Lee [25]. The onset of mass loss around 430 K was taken to indicate the beginning of thermal decomposition. This temperature indicating mass loss was commonly believed to indicate high-temperature phenomena caused by thermal decomposition. This change might to be related to the loss of H_2O suggested by Lee [14].

Solid-state NMR was used to analyze the structure of the protons in $\text{NH}_4\text{H}_2\text{PO}_4$ in a rotating frame. Figure 3 shows the in situ ^1H MAS NMR spectrum of $\text{NH}_4\text{H}_2\text{PO}_4$ as a

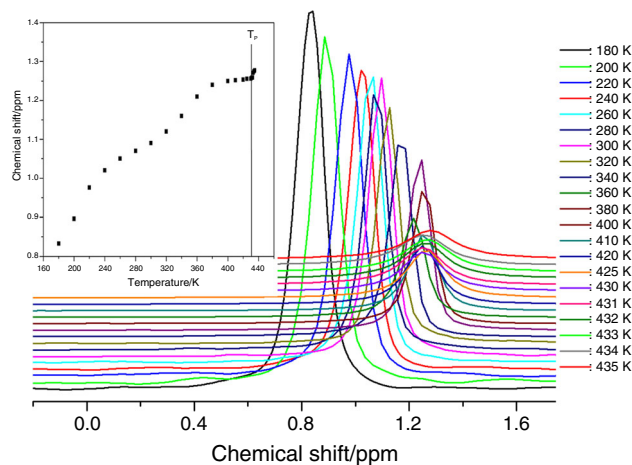


Fig. 5 In situ ^{31}P MAS NMR spectra of $\text{NH}_4\text{H}_2\text{PO}_4$ for different temperatures (Inset chemical shifts of ^{31}P MAS NMR spectrum of $\text{NH}_4\text{H}_2\text{PO}_4$ as a function of temperature)

function of temperature. The ^1H MAS NMR spectrum consists of two peaks at chemical shifts of $\delta = 6.72$ and 15.02 ppm at room temperature. The spinning sidebands are marked with asterisks. The signals at chemical shifts of 6.72 and 15.02 ppm are assigned to the ammonium and hydrogen-bonded protons, respectively. Two types of hydrogen bonds exist in $\text{NH}_4\text{H}_2\text{PO}_4$, as shown in Fig. 1: the ammonium protons (hydrogen-bonded protons in $\text{N}-\text{H}-\text{O}$ between NH_4 and PO_4) and the hydrogen-bonded protons (hydrogen-bonded protons in $\text{O}-\text{H}-\text{O}$ between two PO_4 groups). The strong and weak signals in the spectrum assigned to the ammonium and hydrogen-bonded protons are consistent with the fact that there are four protons in the NH_4 groups and two hydrogen-bonded protons, respectively. The intensity for the hydrogen-bonded protons above 420 K is very weak, and a magnified view of this spectrum is shown in the inset of Fig. 3. The chemical shifts for the ammonium and hydrogen-bonded protons do not change; however, the relative intensities of two signals decrease with increasing temperature (Fig. 4). The relative intensity for two signals decreases somewhat continuously and does not change significantly near T_p .

Structural analysis of the ^{31}P in $\text{NH}_4\text{H}_2\text{PO}_4$ was also performed using ^{31}P MAS NMR. The in situ ^{31}P MAS NMR spectrum for $\text{NH}_4\text{H}_2\text{PO}_4$ is shown in Fig. 5 as a function of temperature. At room temperature, the ^{31}P MAS NMR spectrum shows one signal in $\text{NH}_4\text{H}_2\text{PO}_4$ at a chemical shift of $\delta = 1.09$ ppm with respect to the reference TMS signal. The temperature dependence of the chemical shifts of the ^{31}P NMR signal of $\text{NH}_4\text{H}_2\text{PO}_4$ is shown in the inset in Fig. 5. The ^{31}P chemical shift slowly and monotonically increases with increasing temperature. Therefore, the structural geometry of ^{31}P ions in PO_4 groups of $\text{NH}_4\text{H}_2\text{PO}_4$ changed continuously. Overall, the chemical shift is sensitive to the electrical environment of

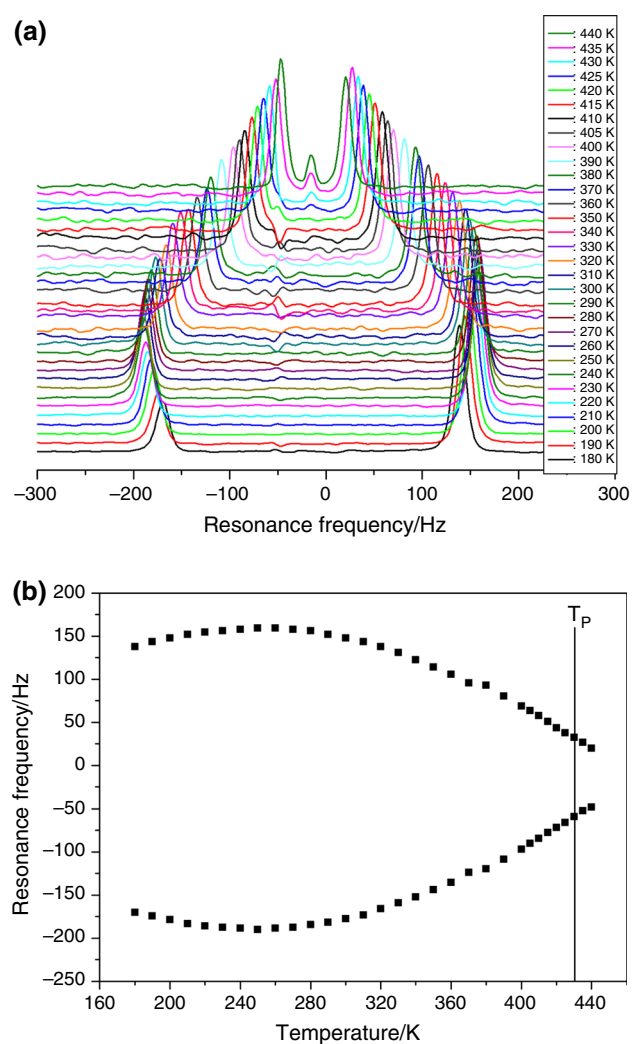


Fig. 6 **a** In situ ^{14}N NMR spectra of $\text{NH}_4\text{H}_2\text{PO}_4$ single crystals for different temperatures and **b** the resonance frequency observed using the ^{14}N NMR spectrum of $\text{NH}_4\text{H}_2\text{PO}_4$ single crystals as a function of temperature

the nucleus. The temperature dependence of the chemical shift is indicative of an electronic instability attributable to a deformation of the PO_4^{3-} tetrahedra.

The NMR spectra of ^{14}N ($I = 1$) in $\text{NH}_4\text{H}_2\text{PO}_4$ single crystals were obtained using static NMR at a Larmor frequency of $\omega_0/2\pi = 43.342$ MHz. The in situ ^{14}N NMR spectra of $\text{NH}_4\text{H}_2\text{PO}_4$ single crystals as a function of temperature are plotted in Fig. 6a. Two resonance lines are obtained owing to the quadrupole interaction of the ^{14}N nucleus. Furthermore, the resonance frequencies of the ^{14}N signals are plotted in Fig. 6b. The resonance frequency increases until 260 K and decreases above 260 K with increasing temperature. Near T_p , they are somewhat

continuous, and the interval between the resonance frequencies is very narrow. Note that these temperature-dependent changes in the ^{14}N resonance frequencies are generally attributed to changes in the structural geometry near $T_p = 430$ K. Here, the electric field gradient (EFG) tensors at the N sites are varied, reflecting the changing atomic configurations around the ^{14}N nuclei.

Conclusions

The structural behavior of $\text{NH}_4\text{H}_2\text{PO}_4$ near the characteristic temperature T_p was studied by examining the chemical shift and resonance frequency using MAS NMR and static NMR, respectively. At high temperature, the changes occurring in the chemical shift and resonance frequency were associated with changes in the atomic positions for two types of hydrogen bonds, phosphorus ions, and nitrogen ions. From these results, the symmetries of the environments of the N–H–O bonds and O–H–O bonds are varied and were related to the structural change of the tetrahedral PO_4 groups and NH_4 groups in the crystal structure.

The chemical shift and resonance frequency do not exhibit anomalous behavior near the characteristic temperature T_p . In order to understand the high-temperature phenomena around T_p in $\text{NH}_4\text{H}_2\text{PO}_4$ crystal, the TG curve was obtained as a function of temperature. The high-temperature phase transformation around T_p was replaced by the onset of partial polymerization at reaction sites on the surface; the mass of $\text{NH}_4\text{H}_2\text{PO}_4$ decreases at 430 K (T_d), which is interpreted as the onset of partial thermal decomposition. The mass loss in the sample observed in the TG curve suggests that T_p is not related to physical changes such as structural phase transition, but is rather related to a chemical change through thermal dehydration, as suggested by Torijano et al. [23] and Park et al. [24, 26]. These discrepancies among different research groups are apparently caused by a difference in experimental humidity conditions and crystal growth conditions. The observed change of symmetry of the crystal suggests a phase-transition-like phenomenon called high-temperature phase transformation at the characteristic temperature $T_p = 430$ K.

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