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Role of NH₄ ions in successive phase transitions of perovskite type $(NH_4)_2ZnX_4$ (X = Cl, Br) by ¹H MAS NMR and ¹⁴N NMR

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The ¹H chemical shifts and the spin-lattice relaxation time, $T_{1\rho}$, in the rotating frame of (NH₄)₂ZnX₄ (X = Cl, Br) are observed in order to investigate local phenomena related to successive phase transitions. The temperature dependence of $T_{1\rho}$ values for ¹H showed a minimum, and the $T_{1\rho}$ values for ¹H appeared to be governed by tumbling molecular motions at high temperatures. In addition, ¹⁴N NMR spectra are studied in each phase of (NH₄)₂ZnX₄ single crystals in the laboratory frame. The phase transition temperatures strongly affect the ¹⁴N number of symmetry related nitrogen centers within the unit cell. The ¹H MAS NMR and ¹⁴N NMR results are discussed to elucidate the roles of NH₄ ions during the phase transitions of (NH₄)₂ZnX₄.

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1. Introduction

Perovskite A_2BX_4 type (A = NH₄, K, Rb, Cs; B = Zn, Co, Cu, Fe, Zn, Cd; X = Cl, Br) crystals have received a great deal of attention because of their nonlinear optical properties, and also because of the significant diversity of their structural phase transitions.¹⁻¹⁰ The prototype of the crystal structures of this family is that of β -K₂SO₄, which consists of isolated BX₄²⁻ tetrahedra and monovalent A⁺ cations placed in two inequivalent cavities. Ammonium tetrachlorozincate, (NH₄)₂ZnCl₄, and ammonium tetrabromozincate, (NH₄)₂ZnBr₄, belong to the family of crystals of the perovskite A₂BX₄ type and are known to undergo several phase transitions. Although the physical properties of (NH₄)₂ZnCl₄ and (NH₄)₂ZnBr₄ have been studied by several research groups, the structural geometry changes during the phase transitions of the two compounds have not been fully understood. Here, the phase transition temperatures and dynamics of the cations in $(NH_4)_2 ZnCl_4$ and $(NH_4)_2 ZnBr_4$ are important. The potential applications of these materials are strongly affected by the phase transitions and dynamics of the cations.11

 $(NH_4)_2ZnCl_4$ undergoes five phase transitions: those between phases I and II at 406 K (= T_{C1}) and phases II and III at 364 K (= T_{C2}) are well-known, and the successive phase transitions at 319 K (= T_{C3}), 271 K (= T_{C4}), and 266 K (= T_{C5}) have also been reported;¹²⁻¹⁴ the phases involved in these transitions are denoted by VI, V, IV, III, II, and I in order of increasing temperature, as shown in Table 1. The structure of (NH_4)₂ZnCl₄ in the normal phase, phase I (above 406 K), is orthorhombic with $a_0 = 9.274$ Å, $b_0 = 12.620$ Å, and $c_0 = 7.211$ Å, and space group *Pnma*.¹² Upon cooling, there is a phase transition at 406 K to an incommensurate phase that is stable down to 364 K.¹⁵ The structure in phase III between 364 K and 319 K is orthorhombic with $a = a_0$, $b = b_0$, $c = 4c_0$, and the space group *Pn2*₁a.^{12,16,17} The room temperature phase, phase IV, is antiferroelectric with a pseudo-orthorhombic monoclinic structure and space group *Pa*.¹² The region between 271 K and 266 K is mixed phase.¹⁴ Below 266 K, the lattice is constant with an orthorhombic structure, where $a = a_0$, $b = b_0$, and $c = 3c_0$.^{12,17}

On the other hand, the successive phase transitions of $(NH_4)_2ZnBr_4$ have been reported at 216 K ($=T_{C3}$), 395 K ($=T_{C2}$), and 432 K ($=T_{C1}$),^{18–20} as shown in Table 1; the phases involved in these transitions are represented by IV, III, II, and I in order of increasing temperature. The structures of $(NH_4)_2ZnBr_4$ crystals in phases I, III, and IV are shown in Fig. 1. In phase I (above 432 K), the structure of $(NH_4)_2ZnBr_4$ is orthorhombic with $a_0 =$ 7.649 Å, $b_0 = 13.353$ Å, $c_0 = 9.727$ Å, and space group *Pmcn*.^{21,22} Upon cooling, there is a phase transition at 432 K to an incommensurate phase II that is stable down to 395 K. The structure in phase III, between 395 K and 216 K, is monoclinic with $a = a_0$, $b = b_0$, $c = 4c_0$, $\beta = 90.00(3)^\circ$, and space group $P2_1/c11.^{22}$ The low-temperature phase IV is orthorhombic with $a = a_0$, $b = b_0$, $c = 3c_0$, and space group $P2_1/cn.^{22}$

The ¹H spin-lattice relaxation times of $(NH_4)_2 ZnCl_4$ and $(NH_4)_2 ZnBr_4$ crystals have been obtained in the laboratory frame by Lim *et al.*²³⁻²⁵ and Ramesh *et al.*,²⁶ respectively. The molecular dynamics and phase transitions of $(NH_4)_2 ZnCl_4$ single crystals were reported previously. There were two crystallographically inequivalent NH₄ sites, namely NH₄(1) and NH₄(2), in the $(NH_4)_2 ZnCl_4$. The ¹H spin-lattice relaxation time T_1 in the laboratory frame was observed to vary continuously with temperature without jumps or changes. The ¹H T_1 passes

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Table 1 Phase transition temperatures, crystal structures, space groups, and lattice constants of (NH ₄) ₂ ZnX ₄ (X =	= Cl, Br)
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$(NH_4)_2 ZnCl_4$						
Transition temperature	$T_{\rm C5}$ (=26	6K) $T_{C4} (=271 \text{ K})$	$T_{\rm C3}$ (=319 k	$T_{C2} (=364 \text{ K})$	<i>T</i> _{C1} (=406 K)	
Phase Structure Space group Lattice constant	VI Orthorhombic $Pna2_1$ $a = a_0$ $b = b_0$ $c = 3c_0$	V Mixed phase	IV Monoclinic Pa $a = a_{o}$ $b = b_{o}$ $c = 4c_{o}$ $\beta = 89.992^{\circ}$	III Orthorhombic $Pn2_1a$ $a = a_0$ $b = b_0$ $c = 4c_0$	II Incommensurate	I Orthorhombic Pnma $a_{o} = 9.274 \text{ Å}$ $b_{o} = 12.620 \text{ Å}$ $c_{o} = 7.211 \text{ Å}$
Reference	Z = 12 12 and 17	Z = 12, 14, 16	Z = 16	Z = 16 12, 16 and 17	15	Z = 4 12
$(NH_4)_2ZnBr_4$						
Transition temperature		T _{C3} (=216 К)	T_{C2}	(=395 K)	$T_{\rm C1}$ (=432 K)	
Phase Structure Space group Lattice constant	Г С <i>F</i> а b с	V Drthorhombic 2_1cn $z = a_0$ $z = b_0$ $z = 3c_0$	III Monoclinic $P2_1/c11$ $a = a_0$ $b = b_0$ $c = 4c_0$ $\beta = 90.00(3)^\circ$	II Incomn	nensurate	I Orthorhombic <i>Pmcn</i> $a_{o} = 7.649 \text{ Å}$ $b_{o} = 13.353 \text{ Å}$ $c_{o} = 9.727 \text{ Å}$
Reference	2 2	T = 12 2	Z = 16 22	20		Z = 4 21 and 22

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through a minimum value near 220 K; the presence of this minimum was attributed to the reorientation of the NH₄ groups. In addition, the ¹⁴N nuclear magnetic resonance (NMR) results in phase I of $(NH_4)_2 ZnCl_4$ were reported for the two inequivalent sites N(1) and N(2): the quadrupole coupling constant, $e^2 q Q/h$, and asymmetry parameter, η , were $e^2 q Q/h = 105.5$ kHz and $\eta = 0.96$ for N(1), and $e^2 q Q/h = 48.2$ kHz and $\eta = 0.087$ for N(2).²⁷

The NMR method enables the study of a lattice's local properties, and is particularly useful in those cases that require information on the behavior of individual structural groups. Measurements of $T_{1\rho}$ obtained by magic angle spinning (MAS) NMR in the rotating frame are advantageous in that they allow for probing of molecular motion in the kHz range, whereas T_1 values obtained by state NMR in a laboratory frame reflect motion in the MHz range.²⁸

The aim of this paper is to clarify the structural changes associated with the successive phase transitions in $(NH_4)_2ZnX_4$ (X = Cl, Br). Detailed studies of the molecular motions are necessary in order to explain the mechanisms of the phase transitions of $(NH_4)_2ZnX_4$. The temperature dependences of the MAS NMR spectra and the spin-lattice relaxation times, $T_{1\rho}$, in the rotating frame for the ¹H nuclei in $(NH_4)_2ZnX_4$ were investigated using a pulsed NMR spectroscopy. In addition, the ¹⁴N NMR spectra in $(NH_4)_2ZnX_4$ single crystals were obtained by static NMR in the laboratory frame, as a function of temperature. The ¹H MAS NMR and ¹⁴N static NMR results were analyzed to elucidate the roles of NH_4 ions during the phase transitions of $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$. The $T_{1\rho}$ values by ¹H MAS NMR obtained here and the previously reported T_1 values by ¹H static NMR are compared. In addition, the information regarding the structural geometry of nitrogen environments in NH_4^+ is discussed as a function of temperature.

2. Experimental method

Single crystals of $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ were obtained by the slow evaporation of aqueous solutions with the appropriate molar ratios of NH_4Cl and $ZnCl_2$, and NH_4Br and $ZnBr_2$, respectively, at 298 K.^{12,29,30} These single crystals exhibited hexagonal shapes that were transparent and colorless.

¹H MAS NMR spectra and the spin-lattice relaxation times, $T_{1\rho}$, in the rotating frame in $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ were measured in a static magnetic field of 9.4 T and Larmor frequency of $\omega_0/2\pi = 400.13$ MHz, using a Bruker 400 MHz NMR spectroscopy at the Korea Basic Science Institute, Western Seoul Center. The chemical shifts were measured with respect to tetramethylsilane (TMS). Powder samples were placed inside a 4 mm cross-polarization (CP)/MAS probe, and the MAS rate was set to 5 kHz to minimize spinning sideband overlap. ¹H $T_{1\rho}$ values were determined using a $\pi/2-t$ sequence by varying the duration of spin-locking pulses. The widths of the $\pi/2$ pulse used to measure the $T_{1\rho}$ values of ¹H in $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ were 4.35 µs and 3.7 µs, respectively, with the spinlocking field equaling 57.47 kHz and 67.56 kHz.



Fig. 1 Projection of the structure along the a-axis in phases (a) I, (b) III, and (c) IV of (NH₄)₂ZnBr₄ crystal

In addition, the ¹⁴N NMR spectra of the (NH₄)₂ZnCl₄ and (NH₄)₂ZnBr₄ single crystals in the laboratory frame were measured using a Unity INOVA 600 NMR spectroscopy 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 ¹⁴N NMR experiments were performed using a solid echo sequence of $\pi/2-t-\pi/2-t$. The widths of the $\pi/2$ pulse for ¹⁴N in (NH₄)₂ZnCl₄ and (NH₄)₂ZnBr₄ were 4 µs and 3.7 µs, respectively. The measurements of ¹H MAS NMR in the rotating frame and ¹⁴N NMR in the laboratory frame were obtained over the temperature range of 180–430 K. Sample temperatures on MAS NMR and static NMR were held constant within ±0.5 K by controlling the helium gas flow and heater current.

3. Experimental results and discussion

3.1 Phase transition temperatures

The phase transition temperatures for $(NH_4)_2 ZnCl_4$ and $(NH_4)_2$ -ZnBr₄ single crystals have not yet been accurately established, as shown in Fig. 2. Here, the small vertical bars were represented the phase transition temperatures reported by several groups. In the case of $(NH_4)_2 ZnCl_4$, this crystal exhibits three temperature dependence anomalies in the dielectric, thermal, and X-ray diffraction measurements at 270 K, 319 K, and 406 K, respectively, as reported by Matsunaga *et al.*¹³ Furthermore, anomalies characteristic of phase transitions reported by Agarwal *et al.*³¹ have been found in the Raman spectra investigations at 194 K, 266 K, 271 K, 319 K, and 406 K. According to Gillet *et al.*,³² the occurrence of phase transitions at 253 K, 256 K, 319 K, 364 K, and 406 K was also confirmed on the basis of the Brillouin investigation.³² In addition, thermal expansion changes at temperatures of 253 K, 255 K, 323 K, 362 K, and 406 K were reported by Tylczynski *et al.*²⁹ In the case of $(NH_4)_2ZnBr_4$, phase transition temperatures have been reported at 216 K, 395 K, and 432 K by Osaka *et al.*,¹⁸ and an additional phase transition at 365 K was reported by Moskalev *et al.*¹⁵ in their investigation of a $(NH_4)_2ZnBr_4$ crystal using ⁸¹Br nuclear quadrupole resonance (NQR), differential thermal analysis (DTA), and dielectric measurements. Fig. 2 shows that the phase transition temperatures obtained by several experiments are inconsistent for $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$, respectively.

In order to determine the phase transition temperatures for the $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ single crystals obtained here, differential scanning calorimetry (DSC) measurements were taken with a DuPont 2010 DSC instrument at a heating rate of 10 °C min⁻¹. The DSC measurements revealed three endothermic peaks at 270 K, 320 K, and 406 K for $(NH_4)_2ZnCl_4$, and four endothermic peaks at 216 K, 362 K, 396 K, and 432 K for $(NH_4)_2ZnBr_4$, as shown in Fig. 3. These endothermic peaks were related to the phase transitions, and the temperatures were consistent with those previously reported by Matsunaga *et al.*¹³ and Moskalev *et al.*¹⁵ The phase transition temperatures of $(NH_4)_2ZnX_4$ may vary according to the conditions of crystal growth.

3.2 Molecular motion near phase transition temperatures from ¹H MAS NMR

The ¹H MAS NMR spectra in $(NH_4)_2 ZnCl_4$ and $(NH_4)_2 ZnBr_4$ were measured as a function of temperature. At room temperature, $(NH_4)_2 ZnCl_4$ and $(NH_4)_2 ZnBr_4$ showed only one peak each, at



Fig. 2 Phase transition temperatures (K) for $(NH_4)_2ZnX_4$ (X = Cl, Br) reported by several groups.

chemical shifts of $\delta = 6.53$ ppm and $\delta = 6.66$ ppm, respectively, as shown in Fig. 4. The phase transition temperatures of $(NH_4)_2ZnCl_4$ are denoted by solid lines, and those of $(NH_4)_2ZnBr_4$ are denoted dash lines. The chemical shifts of the two materials did not change near the phase transition temperatures. The ¹H chemical shifts of $(NH_4)_2ZnCl_4$ decreased with increasing temperature, whereas the ¹H chemical shift of $(NH_4)_2ZnBr_4$ increased with increasing temperature. From the chemical shift for ¹H, the proton environments in N-H…Cl bond and the proton environments in N-H…Br bond were very different. This difference of chemical shifts was possibly due to the difference between the electron structures of halogen ions.

The decay traces for the ¹H resonance line in $(NH_4)_2 ZnCl_4$ and $(NH_4)_2 ZnBr_4$ are represented by a single exponential function of $M(t) = M(\infty) \exp(-t/T_{1\rho})$, where M(t) is the magnetization as a function of the spin-locking pulse duration *t*, and $M(\infty)$ is the total nuclear magnetization of ¹H at thermal equilibrium.¹⁴ The decay traces for the ¹H nuclei varied with the delay time, and these decay traces also varied depending upon the temperature. The decay traces fitted with the single exponential function for delay times. From the slopes of the decay traces, the ¹H spin-lattice relaxation times, $T_{1\rho}$, in the rotating frame for the $(NH_4)_2$ ZnCl₄ and $(NH_4)_2$ ZnBr₄ were obtained as a function of temperature, as shown in Fig. 5. The $T_{1\rho}$ values of ¹H were significantly different in the high-temperature and lowtemperature regions. The significant difference in the T_{10} values indicates that (NH₄)₂ZnCl₄ and (NH₄)₂ZnBr₄ are strongly affected, which considered to be mainly the result of molecular motions. The ¹H T_{10} data showed no evidence of a change near the phase transition temperatures. The trend of ¹H $T_{1\rho}$ in $(NH_4)_2$ ZnCl₄ resembled that of ¹H $T_{1\rho}$ in $(NH_4)_2$ ZnBr₄. The two T_{1p} series displayed similar trends, both decreasing quickly above 310 K. The variation of $T_{1\rho}$ with temperature exhibited a shallow minimum of 7.2 ms at 430 K in the case of $(NH_4)_2$ -ZnBr₄, indicating that distinct molecular motion is present. The T_{10} minimum is considered to be clearly attributable to the tumbling motion of NH_4^+ ions. The $T_{1\rho}$ values are related to the corresponding values of the rotational correlation time, $\tau_{\rm C}$,



Fig. 3 Differential scanning calorimetry (DSC) thermograms of $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ single crystals.



Fig. 4 Chemical shifts of ¹H MAS NMR spectra in $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ as a function of temperature $((NH_4)_2ZnCl_4$: solid lines, $(NH_4)_2ZnBr_4$: dash lines).

which directly measures the rate of motion. The experimental $T_{1\rho}$ value can be expressed in terms of $\tau_{\rm C}$ using molecular motion, as suggested by the Bloembergen–Purcell–Pound (BPP) theory.³³ The $T_{1\rho}$ value in the rotating frame can also be expressed in terms of $\tau_{\rm C}$ using molecular motion.^{28,34}

$$\frac{1}{T_{1\rho}} = (n/20)(\gamma_{\rm H}\gamma_{\rm N}\hbar/r_{\rm H-N}^{3})^{2}[4f(\omega_{\rm I}) + f(\omega_{\rm H} - \omega_{\rm N}) + 3f(\omega_{\rm N}) + 6f(\omega_{\rm H} + \omega_{\rm N}) + 6f(\omega_{\rm H})]$$
(1)

Here:

$$f(\omega_{\rm I}) = \tau_{\rm C} / [1 + \omega_{\rm I}^2 \tau_{\rm C}^2]$$

$$f(\omega_{\rm H} - \omega_{\rm N}) = \tau_{\rm C} / [1 + (\omega_{\rm H} - \omega_{\rm N})^2 \tau_{\rm C}^2]$$

$$f(\omega_{\rm N}) = \tau_{\rm C} / [1 + \omega_{\rm N}^2 \tau_{\rm C}^2]$$

$$f(\omega_{\rm H} + \omega_{\rm N}) = \tau_{\rm C} / [1 + (\omega_{\rm H} + \omega_{\rm N})^2 \tau_{\rm C}^2]$$

$$f(\omega_{\rm H}) = \tau_{\rm C} / [1 + \omega_{\rm H}^2 \tau_{\rm C}^2]$$

In the equation, $\gamma_{\rm H}$ and $\gamma_{\rm N}$ are the gyromagnetic ratios for the ¹H and ¹⁴N nuclei, respectively; *n* is the number of directly bound protons; $r_{\rm H-N}$ is the H–N internuclear distance; \hbar is the reduced Planck constant; $\omega_{\rm H}$ and $\omega_{\rm N}$ are the Larmor frequencies of ¹H and ¹⁴N, respectively; and ω_{1} is the spin-lock field frequency of 67.56 kHz. Here, the $f(\omega_{1})$ is non-zero, *i.e.*, the $\tau_{\rm C}$ is much less than the Larmor frequencies, therefore all of the other terms is far smaller than the $f(\omega_{1})$ term. We analyzed our data by assuming that $T_{1\rho}$ would show a minimum when $\omega_{1}\tau_{\rm C} =$ 1, and that the relation between $T_{1\rho}$ and the characteristic frequency of motion, $1/\tau_{\rm C}$, could be applied. The coefficient in eqn (1) can be determined because the $T_{1\rho}$ curve displays a minimum and because the value of $\tau_{\rm C}$ can be obtained from $\omega_{1}\tau_{\rm C} = 1$; thus, $(n/20)(\gamma_{\rm H}\gamma_{\rm N}\hbar/r_{\rm H-N}^{-3})^{2} \approx 4.66 \times 10^{6}$ in the BPP



Fig. 5 Temperature dependences of the spin-lattice relaxation time, $T_{1\rho}$, in the rotating frame and the spin-lattice relaxation time, T_1 , in the laboratory frame of the ¹H nuclei in (NH₄)₂ZnCl₄ and (NH₄)₂ZnBr₄ ((NH₄)₂ZnCl₄: solid lines, (NH₄)₂ZnBr₄: dash lines).

formula. We were then able to calculate the correlation time $\tau_{\rm C}$ as a function of temperature. The temperature dependence of $\tau_{\rm C}$ follows a simple Arrhenius expression:^{34,35}

$$\tau_{\rm C} = \tau_{\rm o} \exp(-E_{\rm a}/RT), \qquad (2)$$

where τ_0 is a pre-exponential factor, *T* is the temperature, *R* is the gas constant, and E_a is an activation energy. Thus, the slope of the linear portion of a semi-logarithmic plot should yield E_a . The value of E_a for the tumbling motion can be obtained from a plot of log τ_C versus 1000/*T*. We obtained $E_a = 36.69 \pm$ 0.66 kJ mol⁻¹ for the tumbling motion of ¹H in (NH₄)₂ZnBr₄ at high temperature. This value is very similar to that for ¹H in (NH₄)₂ZnCl₄, and is the same within the error range. And, the E_a for (NH₄)₂ZnCl₄ and (NH₄)₂ZnBr₄ at low temperature is 0.32 ± 0.30 kJ mol⁻¹ and 2.25 ± 0.37 kJ mol⁻¹, respectively.

On the other hand, the ¹H spin-lattice relaxation time T_1 in the laboratory frame in $(NH_4)_2ZnCl_4$ previously reported was obtained as a function of temperature, as shown in Fig. 5.^{23–25} In the high temperature region, T_1 increases monotonically with temperature, and T_1 was continuous at the phase transition temperatures. However, the T_1 undergoes a change in slope near T_{C4} . ¹H T_1 passes through a minimum value in the vicinity of 220 K, and the presence of this minimum was attributed to the effects of molecular motion. The relaxation process from the ¹H T_1 curve was affected by molecular motion, as described by the BPP theory.³³ The activation energy in the low and high temperatures was reported 29.95 ± 0.85 kJ mol⁻¹ and 10.99 ± 0.37 kJ mol⁻¹, respectively.

3.3 Structural changes near phase transition temperatures from ¹⁴N NMR

In order to investigate local phenomena related to successive phase transitions, the NMR spectra of ¹⁴N (I = 1) was obtained as a function of temperature using static NMR at a Larmor frequency of $\omega_0/2\pi = 43.342$ MHz. ¹⁴N (I = 1) NMR is a sensitive method for probing local structural properties in each phase. The ¹⁴N NMR spectra consisted of pairs of lines at frequencies corresponding to the transitions $\Delta m = \pm 1 \leftrightarrow \Delta m = 0$. The crystal was oriented such that the magnetic field was aligned with the crystallographic c-axis. Temperature-dependent changes in the ¹⁴N resonance frequency are generally attributed to changes in the structural geometry, indicating a change in the quadrupole coupling constant of the ¹⁴N nuclei. The ¹⁴N NMR spectra at phase I, II, III, IV, and VI in (NH₄)₂ZnCl₄ crystals were plotted in Fig. 6. Here, the ¹⁴N peaks positions were denoted by close circles. Two resonance lines were expected because of the quadrupole interaction of the ¹⁴N nucleus. However, many resonance lines were observed, and they were much narrower in line width.

The resonance frequencies of ¹⁴N signals in $(NH_4)_2ZnCl_4$ and $(NH_4)_2ZnBr_4$ single crystals are respectively plotted in Fig. 7(a) and (b) as a function of temperature. In the case of $(NH_4)_2ZnCl_4$, the phase transitions occurring at T_{C1} , T_{C3} , and T_{C4} were observed from our DSC results, whereas those at T_{C2} and T_{C5} were not observed. Therefore, T_{C1} , T_{C3} , and T_{C4} are denoted by solid lines, and T_{C2} and T_{C5} are denoted dotted lines in Fig. 7(a).



Fig. 6 ¹⁴N NMR spectra in (NH₄)₂ZnCl₄ single crystal at phase I, II, III, IV, and VI.

The resonance frequencies near T_{C1} , T_{C4} , and T_{C5} changed, whereas those near T_{C2} and T_{C3} did not change. In phase I, each unit cell contains four formula units, and there are also two different kinds of ¹⁴N nuclei, termed N(1) and N(2). Therefore, the ¹⁴N NMR spectra exhibited eight resonance lines in four pairs. Here, the two inequivalent sites N(1) and N(2) are distinguished by the quadrupole coupling constant previously reported: $e^2qQ/h = 105.5$ kHz and $\eta = 0.96$ for N(1), and e^2qQ/h = 48.2 kHz and $\eta = 0.087$ for N(2).²⁷ Additional lines in phases II, III, and IV were obtained, although they exhibited very small intensities compared with phase I. In phases III and IV, the unit cell is quadrupoled along the *c*-direction of phase I. The unit cell of phases III and IV contains 16 formula units, and thus 32 resonance lines of 16 pairs are expected. According to the crystallography results shown in Fig. 1(b), eight atoms N(11), N(21), N(31), and N(41) are surrounded by five Cl atoms, while the other atoms N(12), N(22), N(32), and N(42), which are located between the layers created by the ZnCl₄ tetrahedra, are surrounded by eight Cl atoms. From the NMR spectra results of 16 pairs of ¹⁴N, the approximately 32 resonance lines in phases III and IV were measured, as shown in Fig. 7(a). The 32 resonance lines from the 16 pairs of ¹⁴N in the NH₄ ion were consistent with the previously reported crystallography structure.^{12,16,17} In addition, phase VI, below T_{C5} , contains Z = 12 formula units, N(11), N(12), N(21), N(22), N(31), and N(32), as shown in Fig. 1(c). Therefore, approximately 24 resonance lines



Fig. 7 (a) Resonance frequency of ¹⁴N NMR spectra in $(NH_4)_2 ZnCl_4$ single crystal as a function of temperature. (b) Resonance frequency of ¹⁴N NMR spectra in $(NH_4)_2 ZnBr_4$ single crystal as a function of temperature.

in 12 pairs were obtained. In these results, the splitting of the ¹⁴N resonance lines for seven of the pairs slightly decreased with increasing temperature, whereas those of the ¹⁴N resonance lines for the other five pairs slightly increased with increasing temperature. On the other hand, the resonance frequencies in phases I, II, III, and IV for the case of $(NH_4)_2$ -ZnBr₄ are shown in Fig. 7(b). The ¹⁴N NMR spectra from $(NH_4)_2$ ZnBr₄ could not be easily observed in detail because of their very low intensity. However, the resonance frequencies near T_{C2} and T_{C3} changed discontinuously.

As mentioned above, in the case of $(NH_4)_2 ZnCl_4$, four pairs of lines ascribed to N(1) and N(2) nuclei appeared in phase I, above 406 K. Because the frequency distributions in phase II discontinuously emerged from these high-temperature lines, the notations N(1) and N(2) were not retained. Based on this temperature dependence, the assignment of the resonance lines in phases III and IV are also not denoted. The resonance frequency from phase V cannot be distinguished because of the much narrower temperature range. The resonance frequencies in phase VI, below T_{C4} , changed discontinuously from those of phases V and IV. The changes in the resonance lines near T_{C4} for $(NH_4)_2 ZnCl_4$ and T_{C3} for $(NH_4)_2 ZnBr_4$ also indicated a phase transition where the new phase exhibited orthorhombic symmetry, which equates to a higher degree of symmetry compared with monoclinic symmetry. Abrupt changes in the resonance frequencies for ¹⁴N near the phase transition temperatures are generally attributed to structural phase transitions.

Conclusion

Data on structural geometries near successive phase transition temperatures of $(NH_4)_2 ZnX_4$ (X = Cl, Br) were obtained by ¹H MAS NMR and ¹⁴N NMR as a function of temperature. We studied the molecular motions in $(NH_4)_2 ZnX_4$, based on the ¹H chemical shifts and spin-lattice relaxation time, $T_{1\rho}$, in the rotating frame. The ¹H chemical shifts near the phase transition temperatures for the two materials did not show any drastic change, and this result might be related to proton ordering near the phase transition temperatures. From the ¹H $T_{1\rho}$ results, the activation energies for the tumbling motion of ¹H had very similar values, and the tumbling motion of NH₄⁺ ions occurred within the high-temperature range.

We compared the ¹H MAS NMR in the rotating frame measured here and the previously reported ¹H static NMR results in the laboratory frame^{23–25} for $(NH_4)_2ZnCl_4$. The trends in $T_{1\rho}$ values for ¹H in $(NH_4)_2ZnCl_4$ are different from the trends in the T_1 values. The molecular motion by $T_{1\rho}$ in the rotating frame was dominant at high temperature, whereas that by T_1 in the laboratory frame was dominant at low temperature. The activation energy values extracted from $T_{1\rho}$ and T_1 measurements are different for the molecular motions in the kHz and MHz ranges.

The ¹⁴N NMR spectra exhibited a sudden shift in the ¹⁴N peak positions and number of peaks at the phase transition temperatures. The electric field gradient (EFG) tensors at the N sites varied, reflecting the changing atomic configurations around the ¹⁴N nuclei. This is because the phase transition temperature strongly affect the ¹⁴N number of symmetry related nitrogen centers within the unit cell. Therefore, ¹⁴N NMR provides insight into changes in crystal symmetry and cation reorientation rates induced by heating and phase transitions.

The two crystals have different phase transition temperatures, but seemingly similar phase transition mechanisms. Although $(NH_4)_2ZnX_4$ has different bond lengths in the Zn–X (X = Cl, Br) structure, and different X atomic radii, the different halide ions (X = Cl, Br) do not appear to significantly influence the ¹H relaxation time.

Conflicts of interest

There are no conflicts to declare.

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