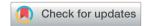
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NMR analysis of structural geometry and molecular dynamics in perovskite-type N(CH₃)₄CdBr₃ crystal near high-temperature phase transition

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The NMR chemical shifts, linewidths, spin-lattice relaxation times in the rotating system T_{1p} , and spin-lattice relaxation times in the laboratory system T_1 were evaluated for the perovskite-type N(CH₃)₄CdBr₃ crystal, aiming to understand the changes in the structural geometry and molecular dynamics from phase I to phase II. From the temperature-dependence of the ¹H, ¹³C, ¹⁴N, and ¹¹³Cd NMR chemical shifts, the structural geometry underwent a continuous change, without anomalous changes around ($T_C=390\,$ K). However, the linewidths in phase I were narrower than those in phase II, indicating that the motional averaging effects were caused by the rapid rotation of the N(CH₃)₄ group. Sudden changes in T_1 and T_{10} were observed near T_C , for which the activation energy E_a in phase I was approximately 12 times larger than that in phase II; the small E_a values in phase II indicate a large degree of freedom for the methyl group and CdBr₆ octahedra, whereas the large E_a in phase I was primarily attributed to the overall N(CH₃)₄ and the ¹¹³Cd in the CdBr₆ groups. Consequently, the phase transition mechanisms of N(CH₃)₄CdBr₃ are related to reorientation of the N(CH₃)₄ group and the arrangement of the CdBr₆ groups.

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Introduction

ABX₃ perovskites are an interesting group of compounds that undergo phase transition accompanied by remarkable changes in their physical and chemical properties.¹⁻⁷ Many studies on organic-inorganic hybrid compounds have yielded meaningful results because of the wide applicability of these materials.8-17 Tetramethylammonium tribromocadmate belongs to the N(CH₃)₄BX₃ (B = 55 Mn, 59 Co, 64 Cu, 65 Zn, 113 Cd; X = ³⁵Cl or ⁷⁹Br) family of ABX₃-type perovskites. ¹⁸⁻²⁹ The crystal structure at room temperature consists of isolated linear chains of face-sharing CdBr₆ octahedra separated by N(CH₃)₄ ions. N(CH₃)₄CdBr₃ has two phase transition temperatures, 160 and 390 K, 19,22,23 with three phases denoted as III, II, and I, respectively, in the order of increasing temperature. The hightemperature transition is a second-order process, whereas the low-temperature transition is a weak first-order phase transition. In phase I (above 390 K), N(CH₃)₄CdBr₃ adopts a hexagonal structure in the space group $P6_3/mmc$ with Z=2. In phase II (below 390 K), the crystal exhibits the same hexagonal structure in space group $P6_3/m$ with Z=2. At room temperature, the crystal structure is hexagonal with lattice constants of a = b = 9.404 Å, c = 6.990 Å, $\alpha = \beta = 90^{\circ}$, and $\gamma = 120^{\circ}.^{20}$ The phase transition at

160 K leads to another hexagonal phase with space group P61 and Z=6. The cell dimensions in phase III are characterized by the

lattice constants a = b = 9.257 Å, c = 20.900 Å, $\alpha = \beta = 90^{\circ}$, and γ

= 120° , ^{24,26} where the *c*-axis is three times longer compared to that in phase II. The structures, space groups, lattice constants, and Z

In a previous study, the ¹H nuclear magnetic resonance

(NMR) spin-lattice relaxation time T_1 in the laboratory frame

did not reveal any anomaly in the temperature range of 77-400 K for N(CH₃)₄CdBr₃. This phenomenon can be explained by

the relaxation mechanism owing to the fast reorientation of the

CH₃ groups. According to a previous report by Baisa et al., 25 a singlet ⁷⁹Br nuclear quadrupole resonance (NQR) spectrum

was obtained for phases II and I, and a triplet spectrum was

in the phases I, II, III are summarized in Table 1.

Table 1 Structures, space groups, lattice constants (\mathring{A}), and Z at phases I, II, and III for N(CH₃)₄CdBr₃

Phase	III	II	I
Structure Space group	Hexagonal <i>P</i> 6 ₁	Hexagonal P6 ₃ /m	Hexagonal P63/mmc
Lattice constants	a = b = 9.257 c = 20.900	a = b = 9.404 c = 6.990	1 0 ₃ /mmc
	$\alpha=\beta=90^{\circ}$	$\alpha=\beta=90^{\circ}$	
Z	$\gamma=120^{\circ}$	$\gamma=120^{\circ}$	2
Reference	24 and 26	20	20

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recorded for phase III. In addition, the NMR T_1 for ⁷⁹Br near 160

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K exhibits strong temperature dependence and changes by three orders of magnitude in the temperature range of 77–310 K. 27 Overall, the relaxation processes of 1 H and 79 Br in N(CH $_{3}$) $_{4}$ CdBr $_{3}$ near the phase-transition temperature of 160 K were studied in the laboratory frame using static NMR. The structural phase transition near the high phase-transition temperature of 390 K presented by our group in the past was briefly studied using magic angle spinning (MAS) NMR in the rotating frame and static NMR in the laboratory frame. 30

Measurements of the spin–lattice relaxation time in the rotating system (T_{1p}) have the advantage of probing the molecular motion within the kHz range, whereas the spin–lattice relaxation time in the laboratory system (T_1) reflects motion within the MHz range.

Although various experimental results have been reported for N(CH₃)₄CdBr₃, the structural geometry and the molecular motion associated with the phase transitions remain undisclosed. This study is expected to provide important insights into the characteristics regarding the advancements in perovskite materials. Therefore, N(CH₃)₄CdBr₃ single crystals are grown, and it was confirmed that the high phase-transition temperature occurs at $(T_{\rm C} = 390 \text{ K})$. The crystal structure is also confirmed to be hexagonal, using single-crystal X-ray diffraction (SCXRD) experiments. The temperature dependence of the ¹H and ¹³C MAS NMR chemical shifts is obtained to elucidate the changes in the structural geometry related to the phase transition. The temperature dependences of the ¹⁴N and ¹¹³Cd NMR chemical shifts near $T_{\rm C}$ in the laboratory system are also measured. In addition, the spin-lattice relaxation times in the rotating system (T_{1p}) for ¹H and ¹³C as a function of temperature are considered, and the corresponding spin-lattice relaxation times in the laboratory system (T_1) for ¹¹³Cd are measured by a static NMR method. Based on these results, the activation energies near the phase-transition temperature of 390 K are discussed in relation to the role of the N(CH₃)₄ group in the cation and Cd in the anion.

2. Experimental

2.1. Crystal growth

Single crystals of $N(CH_3)_4CdBr_3$ were grown by slow evaporation method using $N(CH_3)_4Br$ (Aldrich, 98%) and $CdBr_2$ (Aldrich, 98%) in a molecular weight ratio of 2:1, in an aqueous solution. However, $N(CH_3)_4CdBr_3$ crystals did not grow well at a ratio of 1:1 molar composition. $N(CH_3)_4Br$ and $CdBr_2$ compounds with the ratio of 2:1 were dissolved in distilled water, and stirred and heated at a slightly higher temperature to obtain a completely saturated solution. The single crystals obtained by slow evaporation after a few weeks in a thermostat at 300 K were hexagonal in shape, transparent and colorless with dimensions of $7 \times 3 \times 2$ mm³. To prevent degradation from moisture in the air, the crystals were stored in a desiccator.

2.2. Characterization

Differential scanning calorimetry (DSC) curves were obtained using a DSC instrument at a heating and cooling rate of 10 $^{\circ}$

C min⁻¹ in the 200–570 K range under a flow of dry nitrogen gas. The variation in the crystal morphology with respect to the temperature change was observed using an optical polarizing microscope (Carl Zeiss) on a hot stage (Linkam THMS 600).

The structure and lattice parameters at 250 and 300 K were determined using single-crystal X-ray diffraction (SCXRD) at the Korea Basic Science Institute (KBSI) of the Seoul Western Centre. The crystal was mounted on a diffractometer (Bruker D8 Venture PHOTON III M14) with a graphite-monochromated Mo Kα target and a nitrogen cold stream (-50 °C). Data were collected using the SMART APEX3 and SAINT programs and absorption-corrected using the multiscan method in SADABS. The single-crystal structure was analyzed using direct methods and supplemented with least squares analysis of the entire F^2 matrix using SHELXTL.31 All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were included at geometrically ideal positions. Further, the powder X-ray diffraction (PXRD) patterns were obtained at 300 K and 410 K using an XRD spectrometer with a Mo Kα radiation source by utilizing the SCXRD method.32

NMR spectra of the N(CH₃)₄CdBr₃ crystals were recorded using a solid-state NMR spectrometer (Bruker 400 MHz Avance II+) at KBSI. The ¹H magic angle spinning (MAS) NMR data at the Larmor frequency of $\omega_0/2\pi=400.13$ MHz and the ¹³C MAS NMR data at the Larmor frequency of $\omega_0/2\pi = 100.61$ MHz were measured as a function of temperature. To minimize the spinning sideband, the MAS speed was measured at 10 kHz. ¹H and ¹³C chemical shifts were recorded using tetramethylsilane as the standard. The one-dimensional (1D) NMR spectra of ¹H and ¹³C were obtained with a delay time of 0.5 s. The ¹H and ¹³C spin-lattice relaxation times in the rotating system (T_{1p}) were measured with delay times from 200 μs to 100 ms; a 90° pulse was used for acquiring ¹H and ¹³C data, with a delay of 3.6-3.8 μs. In addition, the static ¹⁴N NMR chemical shift at a Larmor frequency $\omega_{\rm o}/2\pi=28.90$ MHz was monitored with increasing temperature. The 14N NMR chemical shift was determined using NH₄NO₃ as the reference standard, and ¹⁴N NMR spectra were obtained using a solid-state echo sequence. The static NMR spectra for the 113 Cd nucleus at $\omega_{\rm o}/2\pi=88.73$ MHz were obtained using the same NMR spectrometer. The spin-lattice relaxation time in the laboratory system (T_1) was measured by applying the pulse sequence method. A 90° pulse width was used for 113Cd at 4.3 µs. Temperature-dependent NMR spectra were obtained between 180 and 430 K. The temperature was maintained by controlling the N2 gas flow and heater current within an accuracy of ± 0.5 K.

3. Results and discussion

3.1. Single-crystal XRD

SCXRD analysis at 250 and 300 K revealed that N(CH₃)₄CdBr₃ crystallized with a hexagonal structure belonging to space group $P6_3/m$. At 250 K, the lattice parameters are a=b=9.3878 (4) Å, c=6.9957 (5) Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, and Z=2, whereas the lattice constants at 300 K are a=b=9.417 (3) Å, c=7.0002 (3) Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, and Z=2. The crystal structure is composed of isolated linear chains of face-shared CdBr₆

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Br No H

Fig. 1 Projection of the unit cell of hexagonal N(CH₃)₄CdBr₃ at room temperature along the c-axis (big open circle Br in the +z and gray circle Br in -z).

octahedra, which are widely separated by N(CH₃)₄ ions. Here, the bond lengths for C–H are approximately 0.91 Å.²⁶ The single-crystal structure with the chains of CdBr₆ octahedra parallel to the c-axis are shown in Fig. 1.²⁰ Cd²⁺ is at the origin and three Br⁻ ions form a regular triangle. Br on the +z axis is shown as open circles, and Br on the -z axis is shown as gray circles.

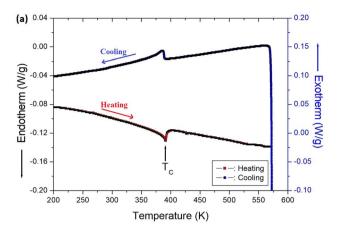
3.2. Phase-transition temperature

DSC analysis of the $N(CH_3)_4CdBr_3$ crystals was performed at a heating and cooling rate of $10\,^{\circ}C$ min⁻¹ with a sample amount of 15.70 mg. The DSC curves show weak endothermic and exothermic peaks near 390 K during heating and cooling, respectively (Fig. 2(a)); the corresponding enthalpy for the peak was 300 J mol⁻¹. The endothermic peak at 390 K corresponds to the phase-transition temperature, arising from the transition from one hexagonal structure to another. The phase transition at this temperature was reversible. Variable-temperature optical polarizing microscopy analysis of the morphology shows that the single crystals did not change until the temperature was increased from 300 to 573 K. The morphologies of the $N(CH_3)_4CdBr_3$ single crystal at (a) 300 K, (b) 350 K, (c) 430 K, and (d) 300 K (after cooling) are shown in the inset of Fig. 2(b).

PXRD analysis was performed below and above the phase-transition temperature, in the 2θ range of 8–60° (Fig. 2(b)). The PXRD pattern recorded at 300 K (blue) differs slightly from that recorded at 410 K (violet). This result correlates well with the endothermic peak obtained from the DSC results; this difference is related to the phase transition temperature, $T_{\rm C}$ (=390 K). The PXRD pattern (dark yellow) obtained after cooling from 410 to 300 K matches well with the results obtained at 300 K before heating. The DSC and PXRD results show that the phase transition is reversible.

3.3. NMR chemical shifts and linewidths for ¹H and ¹³C

Structural analysis was performed by monitoring 1H in $N(CH_3)_4CdBr_3$ using MAS NMR at increasing temperatures. The temperature-dependences of the 1H NMR chemical shifts and linewidths are shown in Fig. 3. At 300 K, the 1H NMR chemical



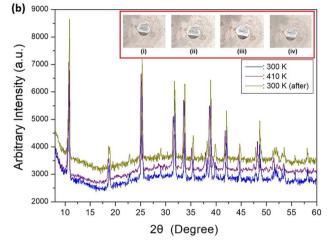


Fig. 2 (a). Differential scanning calorimetry curves at heating and cooling rate of 10 °C min $^{-1}$. (b). The powder X-ray diffraction patterns at 300, 410, and 300 K (after) ((Inset): the morphologies at (i) 300 K, (ii) 350 K, (iii) 430 K, and (iv) 300 K (after cooling) of N(CH $_3$) $_4$ CdBr $_3$ single crystal).

shift appearing at approximately $\delta=3.57$ ppm (inset of Fig. 3) is assigned to the methyl proton. The sidebands for the proton signal obtained at a spinning speed of 10 kHz are indicated by open circles. The ¹H NMR chemical shifts were nearly continuous within the error range, without any anomalous changes near $T_{\rm C}$ as the temperature increased. The full-width-at-half-maximum (FWHM) in the ¹H NMR spectrum increased as the temperature increased and then decreased again rapidly near $T_{\rm C}$; the FWHM decreased from 2 ppm at 300 K to 1.67 ppm near $T_{\rm C}$.

The temperature-dependences of the NMR chemical shifts and 13 C linewidths for N(CH₃)₄CdBr₃ are shown in Fig. 4. The 13 C MAS NMR spectrum at 300 K exhibited one resonance signal (inset of Fig. 4) and a 13 C chemical shift was recorded at 58.82 ppm, related to the methyl carbon. With increasing temperature, the 13 C NMR chemical shift moved from 58.09 to 59.49 ppm without an anomalous change near $T_{\rm C}$, but increased almost linearly with increasing temperature. The continuous change in the NMR chemical shifts due to the local field around the 13 C nuclei indicates changes in the crystallographic geometry, without anomalous changes near $T_{\rm C}$. The 13 C linewidth decreased from 0.35 ppm at 300 K to 0.26 ppm near $T_{\rm C}$, similar

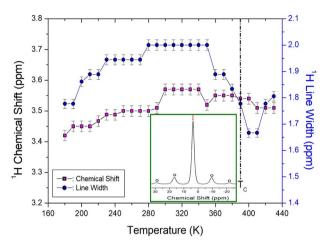


Fig. 3 NMR chemical shifts and line widths for ¹H in N(CH₃)₄CdBr₃ as the temperature rises ((Inset): The ¹H NMR spectrum at 300 K, and open circles are spinning sidebands).

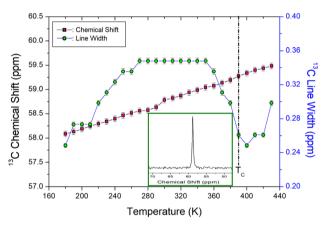


Fig. 4 NMR chemical shifts and line widths for 13 C in N(CH₃)₄CdBr₃ as the temperature rises ((Inset): The 13 C NMR spectrum at 300 K).

to the change in the linewidth of ¹H. This implies that the sources of the interactions between the atoms and ions around the ¹H and ¹³C nuclei are similar. The ¹³C linewidths were very small compared to the ¹H linewidths. The less broadening of the linewidths for ¹H and ¹³C near 160 K are thought to be due to the low phase-transition temperature.

3.4. 1 H and 13 C NMR spin-lattice relaxation times in the rotating system, T_{10}

The changes in the intensity of the 1 H and 13 C NMR signals with variation of the delay times were recorded at a given temperature, and the relationship to the decay rate of the magnetization was defined by the spin-lattice relaxation time, T_{10} : 33,34

$$P(\tau)/P(0) = A \exp(-\tau/T_{10})$$
 (1)

where $P(\tau)$ is the signal intensity at time τ and P(0) is the signal intensity at time $\tau=0$. The ¹H $T_{1\rho}$ and ¹³C $T_{1\rho}$ values for N(CH₃)₄CdBr₃ were obtained from the slope of the intensity ν s. delay time plot using eqn (1). As shown in Fig. 5, the ¹H $T_{1\rho}$ and

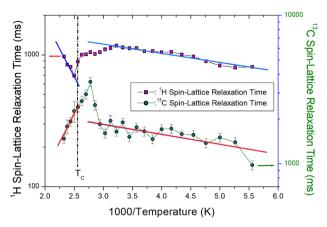


Fig. 5 The spin-lattice relaxation times in the rotating system T_{1p} for ^1H and ^{13}C in N(CH₃)₄CdBr₃ as a function of inverse temperature. The slopes of the solid lines are represented activation energies.

 13 C T_{10} values were of the order of milliseconds, and the 1 H and 13 C $T_{1\rho}$ values slowly increased below $T_{\rm C}$. In contrast, above $T_{\rm C}$, the 13 C T_{10} values, unlike 1 H T_{10} , decreased rapidly. This trend at high temperature is not general, but the activation energy mentioned below is almost the same. Although the distinct proton and carbon dynamics at high temperature are not yet understood, we attribute this result to the disparity between the ¹³C NMR frequency of 100.61 MHz and the ¹H NMR frequency of 400.13 MHz. Furthermore, above $T_{\rm C}$, the molecular motions of ¹H become more constrained, whereas those of ¹³C remain relatively unrestricted. The Arrhenius plots for the T_{10} molecular motions with the relaxation time are separated into fastand slow-motion regions. The fast motion is represented as $\omega_1 \tau_C \ll 1$, $T_{1\rho}^{-1} \alpha \exp(E_a/k_B T)$ and the slow motion as $\omega_1 \tau_C \gg 1$, $T_{1\rho}^{-1} \alpha \omega_1^{-2} \exp(-E_a/k_BT)$. The plot is separated into different motion areas at a temperature that is approximately 50 K lower than the phase transition temperature. At low temperatures, the 1 H T_{10} and 13 C T_{10} values were in the fast-motion region. At high temperatures, the 13 C T_{1p} values were attributed to the slowmotion region, whereas the ${}^{1}H$ $T_{1\rho}$ values were related to the fast-motion region.

Based on Bloembergen–Purcell–Pound (BPP) theory, the experimental values of $T_{1\rho}$ can be expressed by the correlation time $\tau_{\rm C}$ for re-orientational motion, and $T_{1\rho}$ for molecular motion as follows:^{35–37}

$$1/T_{1p} = R\{4\tau_{C}/[1 + \omega_{1}^{2}\tau_{C}^{2}] + \tau_{C}/[1 + (\omega_{C} - \omega_{H})^{2}\tau_{C}^{2}]$$

$$+ 3\tau_{C}/[1 + \omega_{C}^{2}\tau_{C}^{2}] + 6\tau_{C}/[1 + (\omega_{C} + \omega_{H})^{2}\tau_{C}^{2}]$$

$$+ 6\tau_{C}/[1 + \omega_{H}^{2}\tau_{C}^{2}]\} = A \exp(-E_{a}/k_{B}T)$$
(2)

where R is a constant, ω_1 is the spin-locking field, and ω_C and ω_H are the Larmor frequency of 13 C and 1 H, respectively. Local field fluctuations are caused by thermal motion, which is activated by thermal energy. The 1 H and 13 C $T_{1\rho}$ values exhibited similar variations due to similar molecular motions of the C–H bond. $T_{1\rho}$ is generally expressed by an Arrhenius-type equation based on the activation energy (E_a) for molecular motion and temperature. The E_a for 1 H obtained from the slope of the $T_{1\rho}$ vs.

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1000/temperature plot (represented by red squares in Fig. 5) at low and high temperatures was 1.23 \pm 0.10 and 14.87 \pm 2.25 kJ mol⁻¹, respectively. We compared the values of $E_{\rm a}$ for CH₃ and N(CH₃)₄ motion with those reported for similar systems previously. ^{38–42} $E_{\rm a}$ values for methyl group rotation were much smaller than $E_{\rm a}$ for N(CH₃)₄ motions in N(CH₃)₄-based compounds. Small $E_{\rm a}$ values have been reported in other compounds as well; for example, approximately 7.31 kJ mol⁻¹ for p-amphetamine sulfate, ⁴³ about 5 kJ mol⁻¹ for 2 *t*-butyldimethylsilyloxy-6-bromo-naphthalene, ⁴⁴ and 3.8 kJ mol⁻¹ for [N(CH₃)₄]₂SeBr₆. ⁴⁵ $E_{\rm a}$ values for N(CH₃)₄ motion, however, are much larger, ranging from 18 kJ mol⁻¹ to 54 kJ mol⁻¹ for N(CH₃)₄ halides. Therefore, N(CH₃)₄CdBr₃ seems to undergo methyl and N(CH₃)₄ motions below and above $T_{\rm C}$, respectively.

In addition, the $E_{\rm a}$ for $^{13}{\rm C}$ obtained from the slope of T_{1p} vs. 1000/temperature (represented by green circles in Fig. 5) at low and high temperatures was 1.14 ± 0.25 and 16.17 ± 1.83 kJ mol $^{-1}$, respectively. Here, $E_{\rm a}$ is determined at temperatures ranging from 180 to 340 K below $T_{\rm C}$ and from 390 to 430 K above $T_{\rm C}$.

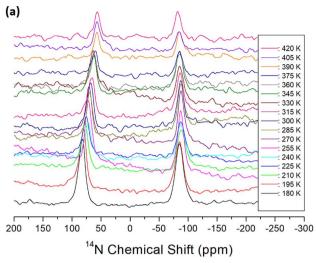
To determine the sample temperature by spinning rate during MAS NMR experiments, the variance between the set temperature and the actual sample temperature inside the probe was previously reported by Guan and Stark. The equation for the fast MAS probe is cited as^{46,47}

$$T_s(f) = 0.98 T_o + 3.79 (^{\circ}\text{C}) \exp(\omega_s/19.6 \text{ kHz}) - 3.49 (^{\circ}\text{C})$$
 (3)

where $T_{\rm o}$ is the set temperature and $\omega_{\rm s}$ is the MAS spinning rate. For example, a set temperature of 360 K for a sample spinning rate of 10 kHz corresponds to 361 K in the fast MAS probe. The temperature variation indicated by DSC and NMR is minimal for the fast MAS probe.

3.5. Static 14N NMR chemical shifts and linewidths

The ¹⁴N static NMR spectra of the N(CH₃)₄CdBr₃ single crystal were obtained with variation of the temperature in the range of 180-420 K using the solid-state echo method. An external magnetic field of 9.4 T was applied to the single crystal in an arbitrary axial direction. The 14N NMR chemical shifts spanned a significantly wider range than the ¹H and ¹³C chemical shifts, suggesting that valuable insight can be gained by considering the surrounding environment of ¹⁴N. Because the spin number of ^{14}N is I=1, the NMR spectrum is expected to have two resonance lines owing to quadrupole interactions.³³ Two ¹⁴N NMR signals appeared on the left and right sides of the zero point of the chemical shifts with variation of the temperature, as shown in Fig. 6(a). At 300 K, 14N NMR signals were recorded at 16.69 and 12.80 ppm. As the temperature increased, the ¹⁴N NMR chemical shifts decreased slightly without any change near $T_{\rm C}$ (Fig. 6(b)); the surrounding environment of ¹⁴N hardly changes as the temperature increases. The reduction in 14N NMR signal intensity with increasing temperature is caused by cross-linking with 13C around the 14N nuclei. The 14N linewidth was broad as approximately 17.30 ppm at low temperatures, and the linewidth as the temperature increased became slightly narrower. As the temperature increased, it was found that



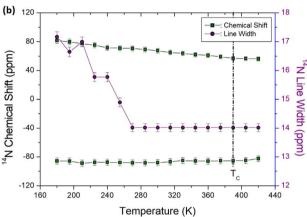


Fig. 6 (a). Static NMR spectrum for 14 N in N(CH₃)₄CdBr₃ single crystal as the temperature rises. (b). Static NMR chemical shifts and line widths for 14 N in N(CH₃)₄CdBr₃ single crystal as the temperature rises.

although there was little change in the ¹⁴N NMR chemical shift, molecular motion due to line width became very active.

3.6. Static 113 Cd NMR chemical shifts and spin-lattice relaxation times in the laboratory system, T_1

The natural abundance and spin number of 113 Cd are 12.3% and I=1/2, respectively; 33,37 the peak has relatively high NMR sensitivity. Therefore, 113 Cd NMR spectroscopy is used to examine the structural geometries and molecular dynamics of various organic and inorganic materials. The NMR spectrum of 113 Cd was recorded for only one resonance line owing to the spin I=1/2. The 113 Cd NMR spectrum at 200 K is shown in the inset of Fig. 7. The 113 Cd NMR chemical shift was recorded using CdCl₂O₈·6H₂O as a standard. The 113 Cd NMR chemical shifts decreased as the temperature increased, and then increased slightly near $T_{\rm C}$. Above $T_{\rm C}$, the chemical shifts moved downfield, indicating that the surrounding environment of 113 Cd changed slightly near $T_{\rm C}$.

The saturation recovery traces for the ¹¹³Cd spectrum of the N(CH₃)₄CdBr₃ single crystal were measured using a static NMR

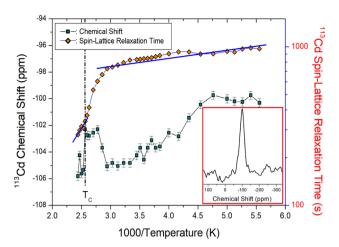


Fig. 7 Static NMR chemical shifts and spin–lattice relaxation times in the laboratory system T_1 for 113 Cd in N(CH $_3$) $_4$ CdBr $_3$ single crystal as a function of inverse temperature. The slopes of the solid lines are represented activation energies ((Inset): The 113 Cd NMR spectrum at 200 K).

method; the recovery traces were satisfactorily fitted to a single-exponential function:³⁰

$$P(\infty) - P(\tau)/P(\infty) = A \exp(-\tau/T_1)$$
 (4)

where $P(\tau)$ is the nuclear magnetization at time τ . The recovery traces for the resonance line of the ¹¹³Cd nuclei were measured by changing the delay times, and the ¹¹³Cd T_1 values in the laboratory frame were obtained from the slope of the intensity versus delay time plot using eqn (4). The T_1 values are represented as functions of the inverse temperature in Fig. 7. Although the slope of the T_1 plot near T_C was roughly continuous, T_1 gradually decreased as the temperature increased, and then decreased rapidly above 340 K; T_1 at 300 K was as long as 825 s, and that at 410 K was shortened to 280 s. At all temperatures measured herein, the ¹¹³Cd T_1 values were in the slowmotion range, where $\omega_C \tau_C \gg 1$, T_1^{-1} a ω_C^{-2} exp $(-E_a/k_B T)$.

The experimental value of T_1 was expressed in terms of the correlation time $\tau_{\rm C}$ for the molecular motions based on the BPP theory:^{35,37}

$$1/T_1 = R\{\tau_C/[1 + \omega_C^2 \tau_C^2] + 4\tau_C/[1 + 4\omega_C^2 \tau_C^2]\} = A \exp(-E_a/k_B T)$$
 (5)

where R is a constant and $\omega_{\rm C}$ is the Larmor frequency of Cd. The T_1 of $^{113}{\rm Cd}$ for thermally activated reorientation follows the usual Arrhenius expression in eqn (5). The $E_{\rm a}$ values were determined from the slope of the semi-log plot of T_1 vs. 1000/ temperature, represented by the orange squares in Fig. 7. The activation energies below and above 340 K were determined to be 1.23 \pm 0.10 kJ mol $^{-1}$ and 11.32 \pm 2.57 kJ mol $^{-1}$, respectively.

4. Conclusion

The data confirm that N(CH₃)₄CdBr₃ crystallizes with a hexagonal structure having a phase transition temperature of 390 K.

The NMR chemical shifts, linewidths, T_{1p} , and T_1 of the perovskite-type N(CH₃)₄CdBr₃ crystal were considered, aiming to understand the structural geometry and changes in the molecular dynamics during the high-temperature transition from phase I to II. Analysis of the ¹H, ¹³C, and ¹⁴N NMR chemical shifts of the cation with temperature showed that the surrounding structural geometry underwent a continuous change, without anomalous changes around $T_{\rm C}$. However, the 113 Cd NMR chemical shifts showed a small change near $T_{\rm C}$. N(CH₃)₄CdBr₃ crystal has a hexagonal structure both above and below the phase transition temperature, and only the space group is different. In relation to this, although the structural geometry changes around ¹H, ¹³C, and ¹⁴N were not significantly detected, the 113Cd NMR chemical shifts are changed slightly near T_C . It is inferred that it is related to the arrangement of Cd in CdBr₃ groups. The linewidths of the ¹H, ¹³C, and ¹⁴N peaks of phase I were narrower than those of phase II, indicating that the motional averaging effects were caused by the rapid rotation of the N(CH₃)₄ group in phase I, resulting from the motional narrowing caused by the rapid rotation of the N(CH₃)₄ groups.

The T_{10} values for the ¹H and ¹³C nuclei, and the T_1 values for ¹¹³Cd were obtained with increasing temperature. The sudden changes in T_1 and T_{10} near T_C indicate a sudden variation in the energy transfer in the area surrounding the protons, carbons, and cadmium. The Ea obtained from the temperaturedependence of T_1 and T_{10} for 1 H, 13 C, and 113 Cd was generally \sim 1.2 kJ mol $^{-1}$ below $T_{\rm C}$ and almost 14.5 kJ mol $^{-1}$ above $T_{\rm C}$, for phases I and II, respectively, where the E_a for phase I is ~ 12 times larger than that for phase II. Because the Ea of CH3 is lower than that of N(CH₃)₄, the methyl group moves more easily and freely. The small values of E_a for phase II indicate a large degree of freedom for the methyl group and CdBr₆ octahedra in $N(CH_3)_4CdBr_3$. For phase I, the large values of E_a were primarily attributed to the overall molecular motion of N(CH₃)₄ and ¹¹³Cd in the CdBr₆ groups. These results are supported by the following: the 113 Cd T_1 obtained herein changes rapidly near T_{C_1} and the ⁷⁹Br NQR spectrum reported by other groups²⁵ also changes rapidly near $T_{\rm C}$. Consequently, the phase-transition mechanisms of N(CH₃)₄CdBr₃ at high temperature are related to the reorientation of the N(CH₃)₄ group and arrangement of ¹¹³Cd in the octahedral CdBr₆ groups. The results of this study on organic-inorganic hybrid perovskite-type N(CH₃)₄CdBr₃ are expected to facilitate their potential applications in various electrochemical devices such as supercapacitors, batteries, and fuel cells. In the future, this study may be able to provide a complete link between the structure, dynamics and NMR properties observed here by combining Ab initio molecular dynamics NMR calculations. 48,49

Author contributions

A. R. Lim performed crystal growth, X-ray experiments, and wrote the manuscript. S. H. Kim measured NMR experiments.

Conflicts of interest

There are no conflicts to declare.

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