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I. Introduction

Organic-inorganic compounds based on two-dimensional (2D) hybrid perovskites, particularly $[(C_nH_{2n+1}NH_3)]_2BX_4$ (n = 1, 2, 3, ...;B = Mn, Co, Cu, Zn, Cd; X = Cl, Br) and $[NH_3(CH_2)_n NH_3]BX_4$ (n =2, 3,...), have attracted considerable attention in recent years. The monoammonium $[(C_nH_{2n+1}NH_3)]_2BX_4$ (ref. 1–7) and diammonium $[NH_3(CH_2)_nNH_3]BX_4$ series have been extensively studied owing to their relative stability and potential applications.8-13 The properties and structural phase transitions of organic-inorganic hybrid perovskites are related to their structures and the interaction of cationic units with complex anionic sublattices.14 The phase transitions for diammonium [NH₃(CH₂)_nNH₃]BX₄ compounds have their origin in the dynamics of the cations, in particular from the dynamics of the NH₃ groups forming hydrogen bonds with the halogen atoms of the anion layers and hindered rotational motions of the entire alkyl group around the long molecular axis.10 For B = Mn, Cu, or Cd, the structure consists of the corner shared octahedral $(BX_6)^{2-}$ alternated with organic layers. In contrast, for B = Co or Zn, isolated tetrahedral structures are formed in the inorganic layer (BX₄)²⁻ sandwiched between layers of organic

Thermal, ferroelastic, and structural properties near phase transitions of organic–inorganic perovskite type [NH₃(CH₂)₃NH₃]CdBr₄ crystals

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Hybrid perovskites have potential applications in several electrochemical devices such as supercapacitors, batteries, and fuel cells. Therefore, we studied the thermal behavior and structural dynamics of organic–inorganic hybrid perovskite [(NH₃)(CH₂)₃(NH₃)]CdBr₄ crystals near phase transition temperatures, T_{C2} (=328 K) and T_{C1} (=363 K), which are correlated to the structural dynamics of cations and anions. The structural geometry and molecular dynamics with emphasis on the role of the [(NH₃)(CH₂)₃(NH₃)] cation and CdBr₆ anion were discussed in terms of MAS ¹H NMR, MAS ¹³C NMR, ¹⁴N NMR, and ¹¹³Cd NMR as a function of the temperature. The environments surrounding ¹H, ¹³C, ¹⁴N, and ¹¹³Cd are investigated near T_{C1} and T_{C2} using these results. Spin–lattice relaxation times $T_{1\rho}$ near T_{C1} are consistent with the change of the lattice constant. Shorter $T_{1\rho}$ values at high temperature indicate that ¹H and ¹³C in the organic chains are more flexible at these temperatures. Based on these results, the physicochemical properties of the cation and anion during the III–II–I phase transitions were discussed. This study was conducted to improve the relatively weak thermal stability compared to the high efficiency for a variety of applications.

cations.^{15–23} These compounds have attracted attention owing to the multiplicity of their crystal structures, which is correlated to the structural dynamics of cations and anions. Ferroelasticity is commonly observed in materials with a perovskite crystal structure. Recently, the ferroelastic twin domain observed in organicinorganic hybrid perovskite likewise garnered significant attention.^{24–27} 2D hybrid perovskites are promising for a variety of applications, including photovoltaics, photocatalysis, batteries, and energy storage.^{28,29}

The [NH₃(CH₂)₃NH₃]CdBr₄ (1,3-propanediammonium tetrabromocadmate) crystal (n = 3; B = Cd; X = Br), a member of the diammonium $[NH_3(CH_2)_nNH_3]BX_4$ series, belongs to the orthorhombic structure at room temperature. This crystal with Cd is a very special case; it exhibits an unusual phase sequence, *i.e.*, its stable phase at the highest temperature is the one with the lowest symmetry.³⁰ This crystal undergoes two phase transitions, at temperatures of 326 K (= T_{C2}) and 368 K (= T_{C1}).^{10,30} The room temperature phase III was determined in the space group *Pnma* (point group *mmm*) of the orthorhombic structure. Its lattice constants have been reported as a = 7.721 Å, b =19.054 Å, c = 7.898 Å, and Z = 4.30 In this phase, Cd atoms are surrounded by six bromine atoms forming a nearly regular octahedron CdBr₆. Of these six bromine atoms, four Br atoms are bridging atoms shared with the neighboring octahedral, and two Br atoms are terminal atoms resulting in bidimensional anion planes. These formations are connected by hydrogen bonds N-H…Br and the cation. The phase II above

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 $T_{\rm C2}$ has the space group *Ima2* (point group *mmm*) and the same orthorhombic structure. In the highest phase I, this crystal is in the monoclinic structure with the space group $P2_1/m$ (point group 2/m). The lattice constants *a* and *b* increase continuously with rising temperature, but the value of *c* decreases slightly at $T_{\rm C2}$ and shortens rapidly at $T_{\rm C1}$. The monoclinic angle β abruptly increases with increasing temperature, reaching approximately 95.5° in this phase, whereas in phases II and III, its value was constant at $\beta = 90^{\circ}.^{30}$

For $[NH_3(CH_2)_3NH_3]CdBr_4$ crystals, a temperature dependence experiment addressing the ^{79,81}Br nuclear quadrupole resonance (NQR) near the phase transition temperatures was studied by Ishihara *et al.*^{31,32} The X-ray structure analysis at room temperature was likewise reported.³² Further, the spectroscopic properties of this crystal with its phase sequence were investigated *via* various experimental methods: differential scanning calorimetry (DSC), infrared (IR), far infrared (FIR), and Raman spectroscopy measurements.¹⁰ Recently, optical and dilatometric studies presented the multidomain states obtained by optical polarizing microscopic observation.¹⁴ Although [NH₃(CH₂)₃NH₃]CdBr₄ has numerous applications, the physicochemical properties and molecular dynamics of its crystals have not been studied to date.

In this study, the structure and phase transition temperatures of [NH₃(CH₂)₃NH₃]CdBr₄ crystals are investigated via X-ray diffraction and DSC. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed to obtain a better understanding of the thermal properties. The chemical shifts and molecular dynamics were probed by ¹H magic-angle spinning nuclear magnetic resonance (MAS NMR) and ¹³C MAS NMR as a function of temperature to elucidate the role of the [NH₃(CH₂)₃NH₃] cation. Furthermore, the chemical shifts for ¹⁴N and ¹¹³Cd of the CdBr₆ anion were recorded by static NMR spectra as a function of the temperature. The spinlattice relaxation times $(T_{1\rho})$ in the rotating frame were discussed in terms of the change of temperature. Based on these results, the structural dynamics of the [NH₃(CH₂)₃NH₃] cation and CdBr₄ anion during the III-II-I phase transitions were discussed. The ferroelastic twin domain walls in all phases were observed as well. Finally, we compare the physicochemical properties of [NH₃(CH₂)₃NH₃]CdBr₄ with those of [NH₃(CH₂)₃-NH₃]CdCl₄ previously reported. Moreover, the physicochemical properties revealed important information regarding the basic mechanisms that enable their widespread applicability.

II. Experimental method

An aqueous solution containing $NH_2(CH_2)_3NH_2 \cdot 2HBr$ and $CdBr_2$ was slowly evaporated at a constant temperature of 300 K to yield single crystals of $[NH_3(CH_2)_3NH_3]CdBr_4$. The $[NH_3(-CH_2)_3NH_3]CdBr_4$ single crystal grown here has a colorless and transparent square shape.

The structure of the $[NH_3(CH_2)_3NH_3]CdBr_4$ crystal at 298 K was analyzed using an X-ray diffraction system equipped with a Cu-K α radiation source. The lattice parameters were determined by single crystal X-ray diffraction at the Western Seoul Center of Korea Basic Science Institute (KBSI). The crystals were

mounted on a Bruker D8 Venture equipped with an I μS microfocus sealed tube Mo-K and a PHOTON III M14 detector.

DSC (TA, DSC 25) experiments were conducted at a heating rate of 10 K min⁻¹ in a temperature range of 200–600 K in nitrogen atmosphere. TGA and DTA experiments were performed on a thermogravimetric analyzer (TA Instrument) in the temperature range of 300–870 K with the same heating rate. The type of fan used in experiment was Al.

The NMR spectra of [NH₃(CH₂)₃NH₃]CdBr₄ crystals were measured on a 400 MHz Avance II+ Bruker solid-state NMR spectrometer at the Western Seoul Center of KBSI. The MAS ¹H and ¹³C NMR experiments were conducted at the Larmor frequencies of 400.13 and 100.61 MHz, respectively. To minimize the spinning sideband, a MAS rate of 10 kHz was employed. Tetramethylsilane (TMS) was used as the standard to record the NMR spectra. $T_{1\rho}$ values were measured using the $\pi/2 - \tau$ sequence method by varying spin-locking pulses. The width of the $\pi/2$ pulse for ¹H and ¹³C was 3.56–3.72 µs. Further, static ¹⁴N NMR and ¹¹³Cd NMR spectra of a [NH₃(CH₂)₃NH₃]CdBr₄ single crystal were measured at Larmor frequencies of 28.90 and 88.75 MHz, respectively, and the chemical shift was referenced with respect to NH₃NO₃ and CdCl₂O₈·6H₂O as standard samples, respectively. The ¹⁴N NMR experiments were performed using a solid-state echo sequence. An almost constant temperature within error range ± 0.5 K was maintained, even when the rate of flow of nitrogen gas and the heater current were adjusted.

The ferroelastic domain pattern in the (001) plane was studied using an optical polarizing microscope. A hot stage (Linkam, THMS 600) and temperature controller maintained the temperature of the crystal.

III. Results and discussion

The X-ray powder diffraction pattern of the $[NH_3(CH_2)_3NH_3]$ CdBr₄ at 298 K are displayed in Fig. 1. And, the lattice constants for $[NH_3(CH_2)_3NH_3]$ CdBr₄ crystal are determined to be a = 7.711



Fig. 1 X-ray diffraction pattern of the $[NH_3(CH_2)_3NH_3]CdBr_4$ crystal at 298 K.

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Fig. 2 Differential scanning calorimetry (DSC) thermogram of [NH₃(-CH₂)₃NH₃]CdBr₄.

 \pm 0.003 Å, *b* = 19.148 \pm 0.008 Å, and *c* = 7.856 \pm 0.004 Å. This result is consistent with that reported previously.30

Three endothermic peaks at 328 K, 363 K, and 557 K were observed in the DSC curves of [NH₃(CH₂)₃NH₃]CdBr₄, as shown in Fig. 2. Two endothermic peaks at 328 K and 363 K are consistent with those previously reported by Staskiewicz et al.30 In order to understand the peak of 557 K, we performed the TGA and DTA experiments and the results are presented in Fig. 3. On the DTA curve, two small endothermic peaks at 328 and 363 K are assigned to the structural phase transitions detected in the DSC experiment. A large endothermic peak at 557 K is assigned to the onset of thermal decomposition temperature $(=T_d)$ by the DTA and a polarizing microscope experiments. This was characterized by a loss in the weight of the compound. It was observed that $[NH_3(CH_2)_3NH_3]CdBr_4$ ($M^w = 508.16$ mg) crystals begin to lose weight as the temperature rises. The amount remaining as solid residue is calculated from the molecular weights and balanced chemical reactions. [NH₃(CH₂)₃NH₃]



Fig. 3 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves for [NH₃(CH₂)₃NH₃]CdBr₄ crystal.



Fig. 4 In situ ¹H MAS NMR spectra for CH₂ and NH₃ of [NH₃(CH₂)₃-NH₃]CdBr₄ at several temperatures. The spinning sidebands are marked with open circles (inset: expansion of ¹H NMR signals above 300 K).

CdBr₄ lost 16 and 32% of its weight at temperatures of approximately 614 and 638 K, respectively. The weight loss can be attributed to the decomposition of HBr and 2HBr moieties, respectively, as shown in Fig. 3. At approximately 850 K, the 98% of the total weight of this crystal is lost.

The temperature-dependent ¹H NMR chemical shifts for [NH₃(CH₂)₃NH₃]CdBr₄ crystals were recorded by MAS NMR, as shown in Fig. 4. Only one resonance signal was observed at low temperature. The observed resonance signal exhibits asymmetric shapes due to overlapping lines of the ¹H for two types of NH_3 and CH_2 in $[NH_3(CH_2)_3NH_3]$ cations. The spinning sidebands were marked with open circles. At 180 K, a single resonance line is present at 7.35 ppm, which subsequently splits into two resonance lines above 300 K (inset Fig. 4).

At 330 K, which is higher than T_{C2} , the NMR spectrum is separated by two resonance lines showing chemical shifts of 7.24 and 3.88 ppm for NH_3 and CH_2 , respectively. The ¹H chemical shifts of NH₃ indicated by dotted lines in Fig. 4 are almost independent of the temperature, while those of CH₂ slightly shift toward the lower side as the temperature increases. From these results, the surrounding environment of H of NH₃ does not change depending on the temperature, and that of H of CH₂ changes slightly according to the temperature.

The ¹H MAS NMR spectrum was measured with respect to several delay times at each temperature. The relationship between the intensities of the NMR signals and the delay times is as follows:33-35

$$I(t) = I(0)\exp(-t/T_{1\rho}),$$
 (1)

where I(t) and I(0) are the signal intensities at times *t* and t = 0, respectively, and T_{10} denotes the spin-lattice relaxation time in the rotating frame. ¹H NMR signals for [NH₃(CH₂)₃NH₃]CdBr₄ at 300 K were recorded by varying the delay times of 0.2-160 ms, as shown in the inset of Fig. 5. The decay curves were fit to Paper



Fig. 5 ¹H NMR spin–lattice relaxation times $T_{1\rho}$ of $[NH_3(CH_2)_3NH_3]$ CdBr₄ as a function of inverse temperature (inset: recovery curves for delay times of ¹H MAS NMR spectrum in $[NH_3(CH_2)_3NH_3]$ CdBr₄ at 300 K).

a single exponential function shown in eqn (1). The T_{10} values of the protons in [NH₃(CH₂)₃NH₃]CdBr₄ were obtained as a function of the inverse temperature, and their results are represented in Fig. 5. The $T_{1\rho}$ values initially increased and then abruptly decreased when the temperature was increased. At 328 K (= T_{C2}), the change in $T_{1\rho}$ values is more or less continuous; however, at approximately 363 K ($=T_{C1}$), there is a slight inflection point, marking a discontinuity. This experimental result is considered to be consistent with previously reported Xray results,³⁰ stating that the *c*-value of the lattice constant is slightly shorter in the vicinity of T_{C2} , but the *c* value is rapidly shortened in the vicinity of T_{C1} . The $T_{1\rho}$ values of the protons in the $[NH_3(CH_2)_3NH_3]$ cation are 10–300 ms over the measured temperature range. At 180 K, T_{10} is approximately 72 ms, and at 290 K, it has a very long duration of 303 ms, and at 430 K, it exhibits a very short duration of 11 ms. The ${}^{1}H T_{1\rho}$ values for NH₃ and CH₂ separated from temperatures above 320 K have highly similar values. The $T_{1\rho}$ values experience fast motion below T_{C2} and slow motion above T_{C2} . The general behavior of the T_{1p} for random motions of the Arrhenius type with a correlation time $\tau_{\rm C}$ is described in three regimes, including both fast and slow motion regimes. The fast motion regime is described as $\omega_1 \tau_C \ll 1$, $T_{1\rho}^{-1} \propto \exp(E_a/k_B T)$, and the slow motion regime as $\omega_1 \tau_C \gg 1$, $T_{1\rho} \propto \omega_1^{-2} \exp(-E_a/k_BT)$, where ω_1 denotes the radiofrequency power of the spin lock pulse, and $E_{\rm a}$ represents the activation energy. Different limits are satisfied for $\omega_1 \tau_C$ in each of the three temperature ranges, separated by $T_{C1} =$ 363 K and $T_{\rm C2} =$ 328 K. Specifically, the limit $\omega_1 \tau_{\rm C} \gg 1$ applies for both $T > T_{C1}$ and $T_{C2} < T < T_{C1}$, and the limit $\omega_1 \tau_C \ll 1$ for $T < T_{C2}$. As indicated by the solid lines in Fig. 5, $E_a = 5.21 \pm 0.38$ kJ mol⁻¹ at temperature below T_{C2} , while above T_{C1} , $E_a = 35.98 \pm 0.68$ kJ mol⁻¹. The decrease in $T_{1\rho}$ values with temperature indicates an increase in proton mobility at higher temperatures.

The ¹³C MAS NMR chemical shifts in $[NH_3(CH_2)_3NH_3]CdBr_4$ were measured with respect to the change in temperature, as shown in Fig. 6. The ¹³C MAS NMR spectrum for TMS was obtained at 38.3 ppm at 300 K. This peak at 38.3 ppm was taken as



Fig. 6 In situ 13 C MAS NMR spectra for CH₂-1 and CH₂-2 of [NH₃(-CH₂)₃NH₃] CdBr₄ as a function of temperature.

the standard and calibrated as a peak at zero ppm. Here, the CH₂ sandwiched between two other CH₂ is labeled as CH₂-1, and the CH₂ close to NH₃ is labeled CH₂-2. At 300 K, the carbon signals corresponding to the CH₂-1 and CH₂-2 in [NH₃(CH₂)₃-NH₃]CdBr₄ appear at 25.55 and 39.96 ppm, respectively. Below T_{C2} , ¹³C resonance signals show two resonance lines for CH₂-1 and CH₂-2. Between T_{C2} and T_{C1} , ¹³C resonance signal was separated into three or four resonance lines. Their resonance lines at temperatures above T_{C1} were again reduced to two. Here, below T_{C2} , the chemical shifts of CH₂-1 and CH₂-2 are shifted slightly upward as the temperature increases, but at temperatures above T_{C1} , the chemical shifts of the two resonance lines are almost independent of the temperature.

The change in the full width at half maximum (FWHM) for ¹³C NMR spectra with respect to the temperature is shown in



Fig. 7 Line widths of ¹³C MAS NMR signal for CH₂-1 and CH₂-2 in $[NH_3(CH_2)_3NH_3]CdBr_4$ as a function of temperature.

Fig. 7. The ¹³C NMR line widths for CH₂-1 and CH₂-2 decreased with an increase in temperature. The line width of the resonance line is approximately 2.8 and 4.5 ppm, respectively, for CH₂-1 and CH₂-2 at low temperature. However, as the temperature increases, the line width changes from a Gaussian to a Lorentzian shape, and it decreases rapidly. In particular, it is markedly reduced near T_{C2} and T_{C1} . The line width decreases with increasing temperature due to internal molecular motion, and that of CH₂-2 is broader than that of CH₂-1.

The intensities of ¹³C MAS NMR signals for CH₂-1 and CH₂-2 in [NH₃(CH₂)₃NH₃]CdBr₄ were measured by varying the delay times at each temperature. The decay curves for CH₂-1 and CH₂-2 were fitted to a single exponential equation in eqn (1). ¹³C T_{10} values were measured by the spin-locking pulse sequence with a locking pulse of 69.44 kHz. From the slope of their recovery traces, the ${}^{13}CT_{1p}$ values were obtained for CH₂-1 and CH₂-2 as a function of 1000/temperature, as shown in Fig. 8. The values of $T_{1\rho}$ are somewhat continuous near T_{C2} , and discontinuous near T_{C1} . Similar to the results of ¹H T_{1p} , the discontinuous change near T_{C1} is consistent with the result of a rapid shortening of the lattice constant c-value. The T_{10} vs. inverse temperature curves shows minima at 32.65 and 29.14 ms for CH2-1 and CH2-2 at 230 K, respectively. This trend indicates that distinct molecular motions exist, where the minimum T_{10} was attributed to the uniaxial rotation of CH_2 ions. The $T_{1\rho}$ values were described by the correlation time $\tau_{\rm C}$ for molecular motion. The $T_{1\rho}$ value for the molecular motion is given by:³⁴

$$I/T_{1\rho} = C(\gamma_{\rm C}^{2}\gamma_{\rm H}^{2}\hbar^{2}h^{2})\{4\tau_{\rm C}/[1+\omega_{1}^{2}\tau_{\rm C}^{2}] + t_{\rm C}/[1+(\omega_{\rm H}-\omega_{\rm C})^{2}\tau_{\rm C}^{2}] + 3\tau_{\rm C}/[1+\omega_{\rm H}^{2}\tau_{\rm C}^{2}] + 6\tau_{\rm C}/[1+(\omega_{\rm H}+\omega_{\rm C})^{2}\tau_{\rm C}^{2}] + 6\tau_{\rm C}/[1+(\omega_{\rm H}^{2}\tau_{\rm C}^{2})]\}$$
(2)

where C is a coefficient, $\gamma_{\rm C}$ and $\gamma_{\rm H}$ are the gyromagnetic ratios for ¹³C and ¹H, respectively, \hbar is the Planck constant, r is the



Fig. 9 Static ¹⁴N chemical shifts of [NH₃(CH₂)₃NH₃]CdBr₄ single crystal as a function of temperature (inset: ¹⁴N chemical shift at 180 K).

distance between the proton and the carbon, $\omega_{\rm H}$ and $\omega_{\rm C}$ are the Larmor frequencies of ¹H and ¹³C, respectively, and ω_1 is the spin-lock field. When $\omega_1 \tau_C = 1$, $T_{1\rho}$ has a minimum value, and the coefficient of eqn (2) is obtained from the relationship between T_{10} and ω_1 . From this coefficient, the $\tau_{\rm C}$ values can be obtained relative to the temperature. The local field fluctuation is governed by the thermal motion of CH2-1 and CH2-2, which is activated by thermal energy. The $\tau_{\rm C}$ is described by Arrhenius behavior: $\tau_{\rm C} = \tau_{\rm o} \exp(-E_{\rm a}/k_{\rm B}T)$, where $\tau_{\rm o}$, $E_{\rm a}$, and $k_{\rm B}$ denote the pre-correlation time, activation energy of the motions, and Boltzmann constant, respectively.³³ As the magnitude of E_a depends on the molecular dynamics, we plotted on a logarithmic scale $\tau_{\rm C} \nu s$. 1000/temperature (inset of Fig. 8). Below $T_{\rm C2}$, $\mathit{E}_{\rm a}$ values for CH₂-1 and CH₂-2 are 13.66 \pm 0.58 and 14.59 \pm 0.72 kJ mol⁻¹, respectively, and above T_{C1} , E_a values for CH₂-1



Fig. 8 13 C NMR spin–lattice relaxation times T_{10} for CH₂-1 and CH₂-2 of [NH₃(CH₂)₃NH₃]CdBr₄ as a function of inverse temperature (inset: the correlation times for CH2-1 and CH2-2 as a function of inverse temperature).



Fig. 10 Static ¹¹³Cd chemical shifts of [NH₃(CH₂)₃NH₃]CdBr₄ single crystal as a function of temperature.



Fig. 11 Ferroelastic domain wall patterns of $[NH_3(CH_2)_3NH_3]CdBr_4$ crystal at (a) phase III (297 K), (b) phase II (333 K), and (c) phase I (383 K).

and CH₂-2 are 30.34 \pm 3.41 and 35.64 \pm 2.16 kJ mol $^{-1},$ respectively.

Static ¹⁴N NMR investigations of [NH₃(CH₂)₃NH₃]CdBr₄ single crystal were conducted over the temperature range of 180-430 K. The ¹⁴N spectra obtained using the solid-state echo method by static NMR is shown in Fig. 9. Two ¹⁴N NMR signals were recorded from the quadrupole interactions due to the spin number I = 1. The lines with the same color below T_{C2} indicate the same pairs for ¹⁴N. Near 328 K (= T_{C2}), the number of resonance lines and chemical shifts of the NMR spectrum showed abrupt changes. The changes in the ¹⁴N chemical shift as a function of temperature were attributed to variations in the structural geometry. The chemical shift of the ¹⁴N signals below T_{C2} exhibited almost continuous change, and it was difficult to observe the N signal due to the wider line width above the T_{C2} temperature. Near T_{C2} , the electric field gradient tensors at N sites varied, reflecting changes in the atomic configuration around the nitrogen atom. The environment around ¹⁴N in the NH_3 groups indicates that the change is large near T_{C2} . Furthermore, at the temperature below T_{C2} , two different ¹⁴N spectra were explained as follows. According to previously

reported X-ray results,³⁰ there are no reports related to two different N sites, whereas there are reports of twin domain observations; therefore, the two different N sites are attributed to the twin domain.

Static ¹¹³Cd NMR experiments were employed to examine the structural environment in CdBr₆ anions of the $[NH_3(CH_2)_3NH_3]$ CdBr₄ single crystal. The spectrum exhibits only one peak due to the spin of I = 1/2. ¹¹³Cd NMR spectra were obtained at several temperatures, as shown in Fig. 10. The NMR chemical shift was recorded using CdCl₂O₈·6H₂O as the standard. At 300 K, the line width is 37.95 ppm. As shown in Fig. 10, the chemical shifts for ¹¹³Cd are almost constant for temperatures increasing from 180 to 410 K. This result indicates that the environment of the Cd atom surrounded by six Br atoms does not change with increasing temperature.

A crystal is ferroelastic when it has two or more orientation states in the absence of mechanical stress, and is capable to shift from one to another by mechanical stress. Several parallel lines representing ferroelastic twin domain walls are present at room temperature phase III (Fig. 11(a)), and we did not observe any changes to the domain pattern in phase II. The symmetry of phase II remains orthorhombic, and the domain wall is preserved (Fig. 11(b)). Similarly, the same domain pattern was observed in the monoclinic phase I (Fig. 11(c)). The twin boundary exists in the same direction at all temperatures. Here, the [NH₃(CH₂)₃NH₃]CdBr₄ crystal exists in two crystallographic phases: monoclinic (2/m) above 363 K, orthorhombic (mmm)between 328 and 363 K, and orthorhombic (mmm) below 328 K. For the transition from the *mmm* of the orthorhombic phase to the 2/m of the monoclinic phase, the domain wall orientations were expressed as x = 0 and z = 0. According to Aizu³⁶ and Sapriel,37 the equations of the twin domain walls are reflected the ferroelasticity of mmmF2/m. In this case, this corresponds to "inverse" mmmF2/m suggested by Prezeslawski et al.,14 unlike the *mmmF2/m* reported by Sapriel. Hence, our results support

Table 1 Structure, space group, lattice constant (Å), phase transition temperature T_C (K), thermal decomposition temperature T_d (K), ¹H spin–lattice relaxation time T_{1p} (ms), and activation energies E_a (kJ mol⁻¹) for ¹H and ¹³C in [NH₃(CH₂)₃NH₃] CdBr₄ and [NH₃(CH₂)₃NH₃]CdCl₄ crystals

	[NH ₃ (CH ₂) ₃ NH ₃]CdBr ₄	[NH ₃ (CH ₂) ₃ NH ₃]CdCl ₄
Structure	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma
Lattice constant	a = 7.711	a = 7.34163
	b = 19.148	b = 19.0300
	c = 7.856	c = 7.49273
T _C	328, 363, 557	375
$T_{\rm d}$	580	520
¹ Η <i>T</i> 1ρ	280.16 (NH ₃ and CH ₃ at 300 K)	411.53 (NH ₃ at 300 K)
		551.12 (CH ₂ at 300 K)
¹³ C <i>Τ</i> 1ρ	81.59 (CH ₂ -1 at 300 K)	37.13 (CH ₂ -1 at 300 K)
	59.80 (CH ₂ -2 at 300 K)	29.13 (CH ₂ -2 at 300 K)
¹ H E _a	35.98 (phase I)	25.36 (phase I)
	5.21 (phase III)	8.37 (phase II)
${}^{13}C E_a (CH_2-1)$	30.34 (phase I)	10.18 (phase I)
	13.66 (phase III)	29.96 (phase II)
${}^{13}\text{C} E_{a} (\text{CH}_{2}\text{-}2)$	35.64 (phase I)	8.45 (phase I)
	14.59 (phase III)	39.94 (phase II)

the mechanism of ferroelastic twin domains. Further, the two types of inequivalent ¹⁴N NMR lines are attributed to the ferroelastic twin domain structure.

IV. Conclusions

We considered the physical properties of organic-inorganic hybrid perovskite [(NH₃)(CH₂)₃(NH₃)]CdBr₄ crystals. First, the structure and phase transition temperatures (328 K and 363 K) were confirmed by X-ray diffraction and DSC experiments, respectively. We found that the TGA curve exhibits stability until 557 K. Second, the ¹H NMR chemical shifts of CH₂ for crystallographic environments changed more significantly with temperature than those for NH_3 . At temperatures below T_{C2} , the ¹³C chemical shifts change to a slightly upward chemical shift, whereas above T_{C1} , the chemical shift hardly changes. Furthermore, the ¹⁴N chemical shift changes with temperature, whereas the ¹¹³Cd chemical shift is independent of it. This is because the environments around N change, while the ¹¹³Cd chemical shifts were not attributed to the rotation of CdBr₆ octahedra. Finally, ¹H T_{10} shows fast motion at low temperature and slow motion at high temperature, while ${}^{13}C$ $T_{1\rho}$ shows molecular motion at low temperature and slow motion at high temperature. Shorter T_{10} values at high temperature indicate that ¹H and ¹³C in the organic chains are more flexible at these temperatures.

We compared the physical properties of the previously reported [(NH₃)(CH₂)₃(NH₃)]CdCl₄ crystals,³⁸ and those of [NH₃(-CH₂)₃NH₃]CdBr₄ examined in this study. This is summarized in Table 1. The decomposition temperature of [NH₃(CH₂)₃NH₃] CdBr₄ is higher than that of $[NH_3(CH_2)_3NH_3]CdCl_4$. In the two compounds, the tendency of the ¹H and ¹³C T_{1p} values in terms of the temperature change is very similar, while their activation energies are very different, as shown in Table 1; [NH₃(CH₂)₃-NH₃]CdBr₄ has a large E_a at high temperatures, whereas $[NH_3(CH_2)_3NH_3]CdCl_4$ has a large E_a at low temperature. Notably, their ¹¹³Cd chemical shifts depend on the temperature change, which indicates the difference between the surrounding environments of CdBr₆ and CdCl₆ octahedra in the two compounds. Although the two crystals contain the same cations, the observed differences in structural dynamics obtained from the chemical shifts and T_{10} values of the two compounds can be attributed to the differences in halogen atoms Br⁻ and Cl⁻ surrounding of Cd. These results provide insights into the molecular dynamics of the [NH₃(CH₂)₃NH₃] CdBr₄ crystals, and are expected to facilitate their potential applications.

Conflicts of interest

There are no conflicts to declare.

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