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# Thermal, ferroelastic, and structural properties near phase transitions of organic–inorganic perovskite type $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$ 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  $[(\text{NH}_3)(\text{CH}_2)_3(\text{NH}_3)]\text{CdBr}_4$  crystals near phase transition temperatures,  $T_{\text{C}2}$  ( $=328$  K) and  $T_{\text{C}1}$  ( $=363$  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  $[(\text{NH}_3)(\text{CH}_2)_3(\text{NH}_3)]$  cation and  $\text{CdBr}_6$  anion were discussed in terms of MAS  $^1\text{H}$  NMR, MAS  $^{13}\text{C}$  NMR,  $^{14}\text{N}$  NMR, and  $^{113}\text{Cd}$  NMR as a function of the temperature. The environments surrounding  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ , and  $^{113}\text{Cd}$  are investigated near  $T_{\text{C}1}$  and  $T_{\text{C}2}$  using these results. Spin–lattice relaxation times  $T_{1\rho}$  were discussed in terms of the change in temperature. The discontinuous changes of  $^1\text{H}$   $T_{1\rho}$  and  $^{13}\text{C}$   $T_{1\rho}$  near  $T_{\text{C}1}$  are consistent with the change of the lattice constant. Shorter  $T_{1\rho}$  values at high temperature indicate that  $^1\text{H}$  and  $^{13}\text{C}$  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.

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## 1. Introduction

Organic–inorganic compounds based on two-dimensional (2D) hybrid perovskites, particularly  $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)]_2\text{BX}_4$  ( $n = 1, 2, 3, \dots$ ;  $\text{B} = \text{Mn}, \text{Co}, \text{Cu}, \text{Zn}, \text{Cd}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) and  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$  ( $n = 2, 3, \dots$ ), have attracted considerable attention in recent years. The monoammonium  $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)]_2\text{BX}_4$  (ref. 1–7) and diammonium  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$  series have been extensively studied owing to their relative stability and potential applications.<sup>8–13</sup> 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.<sup>14</sup> The phase transitions for diammonium  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$  compounds have their origin in the dynamics of the cations, in particular from the dynamics of the  $\text{NH}_3$  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.<sup>10</sup> For  $\text{B} = \text{Mn}, \text{Cu}$ , or  $\text{Cd}$ , the structure consists of the corner shared octahedral  $(\text{BX}_6)^{2-}$  alternated with organic layers. In contrast, for  $\text{B} = \text{Co}$  or  $\text{Zn}$ , isolated tetrahedral structures are formed in the inorganic layer  $(\text{BX}_4)^{2-}$  sandwiched between layers of organic

cations.<sup>15–23</sup> 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 organic–inorganic hybrid perovskite likewise garnered significant attention.<sup>24–27</sup> 2D hybrid perovskites are promising for a variety of applications, including photovoltaics, photocatalysis, batteries, and energy storage.<sup>28,29</sup>

The  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  (1,3-propanediammonium tetrabromocadmate) crystal ( $n = 3$ ;  $\text{B} = \text{Cd}$ ;  $\text{X} = \text{Br}$ ), a member of the diammonium  $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$  series, belongs to the orthorhombic structure at room temperature. This crystal with  $\text{Cd}$  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.<sup>30</sup> This crystal undergoes two phase transitions, at temperatures of 326 K ( $=T_{\text{C}2}$ ) and 368 K ( $=T_{\text{C}1}$ ).<sup>10,30</sup> 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  $Z = 4$ .<sup>30</sup> In this phase,  $\text{Cd}$  atoms are surrounded by six bromine atoms forming a nearly regular octahedron  $\text{CdBr}_6$ . Of these six bromine atoms, four  $\text{Br}$  atoms are bridging atoms shared with the neighboring octahedral, and two  $\text{Br}$  atoms are terminal atoms resulting in bidimensional anion planes. These formations are connected by hydrogen bonds  $\text{N}-\text{H}\cdots\text{Br}$  and the cation. The phase II above

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$T_{C2}$  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  $T_{C2}$  and shortens rapidly at  $T_{C1}$ . The monoclinic angle  $\beta$  abruptly increases with increasing temperature, reaching approximately  $95.5^\circ$  in this phase, whereas in phases II and III, its value was constant at  $\beta = 90^\circ$ .<sup>30</sup>

For  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystals, a temperature dependence experiment addressing the  $^{79,81}\text{Br}$  nuclear quadrupole resonance (NQR) near the phase transition temperatures was studied by Ishihara *et al.*<sup>31,32</sup> The X-ray structure analysis at room temperature was likewise reported.<sup>32</sup> 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.<sup>10</sup> Recently, optical and dilatometric studies presented the multidomain states obtained by optical polarizing microscopic observation.<sup>14</sup> Although  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  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  $^1\text{H}$  magic-angle spinning nuclear magnetic resonance (MAS NMR) and  $^{13}\text{C}$  MAS NMR as a function of temperature to elucidate the role of the  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$  cation. Furthermore, the chemical shifts for  $^{14}\text{N}$  and  $^{113}\text{Cd}$  of the  $\text{CdBr}_6$  anion were recorded by static NMR spectra as a function of the temperature. The spin-lattice 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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$  cation and  $\text{CdBr}_4$  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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  with those of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$  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  $\text{NH}_2(\text{CH}_2)_3\text{NH}_2 \cdot 2\text{HBr}$  and  $\text{CdBr}_2$  was slowly evaporated at a constant temperature of 300 K to yield single crystals of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$ . The  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  single crystal grown here has a colorless and transparent square shape.

The structure of the  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystal at 298 K was analyzed using an X-ray diffraction system equipped with a  $\text{Cu-K}\alpha$  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  $\mu\text{S}$  micro-focus sealed tube  $\text{Mo-K}\alpha$  and a PHOTON III M14 detector.

DSC (TA, DSC 25) experiments were conducted at a heating rate of  $10 \text{ K min}^{-1}$  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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystals were measured on a 400 MHz Avance II+ Bruker solid-state NMR spectrometer at the Western Seoul Center of KBSI. The MAS  $^1\text{H}$  and  $^{13}\text{C}$  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  $^1\text{H}$  and  $^{13}\text{C}$  was 3.56–3.72  $\mu\text{s}$ . Further, static  $^{14}\text{N}$  NMR and  $^{113}\text{Cd}$  NMR spectra of a  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  single crystal were measured at Larmor frequencies of 28.90 and 88.75 MHz, respectively, and the chemical shift was referenced with respect to  $\text{NH}_3\text{NO}_3$  and  $\text{CdCl}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$  as standard samples, respectively. The  $^{14}\text{N}$  NMR experiments were performed using a solid-state echo sequence. An almost constant temperature within error range  $\pm 0.5 \text{ K}$  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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  at 298 K are displayed in Fig. 1. And, the lattice constants for  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystal are determined to be  $a = 7.711$

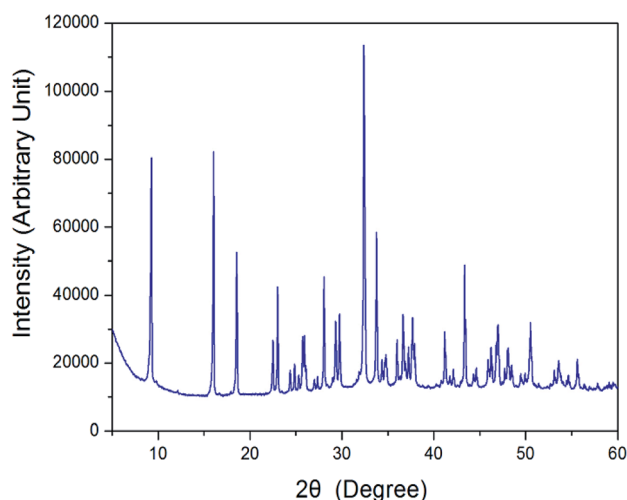


Fig. 1 X-ray diffraction pattern of the  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystal at 298 K.



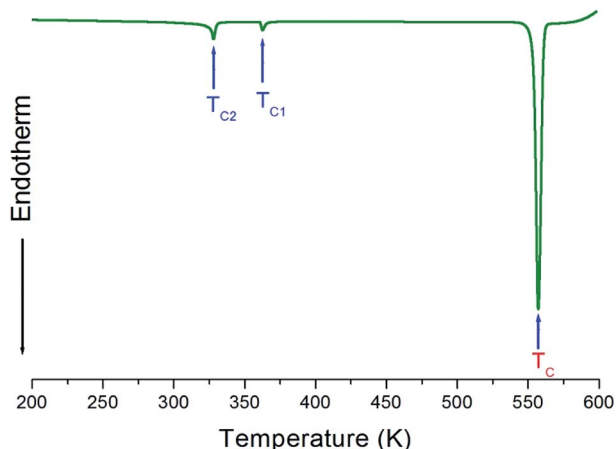


Fig. 2 Differential scanning calorimetry (DSC) thermogram of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$ .

$\pm 0.003 \text{ \AA}$ ,  $b = 19.148 \pm 0.008 \text{ \AA}$ , and  $c = 7.856 \pm 0.004 \text{ \AA}$ . This result is consistent with that reported previously.<sup>30</sup>

Three endothermic peaks at 328 K, 363 K, and 557 K were observed in the DSC curves of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$ , as shown in Fig. 2. Two endothermic peaks at 328 K and 363 K are consistent with those previously reported by Staskiewicz *et al.*<sup>30</sup> 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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  ( $M^w = 508.16 \text{ mg}$ ) 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.  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$

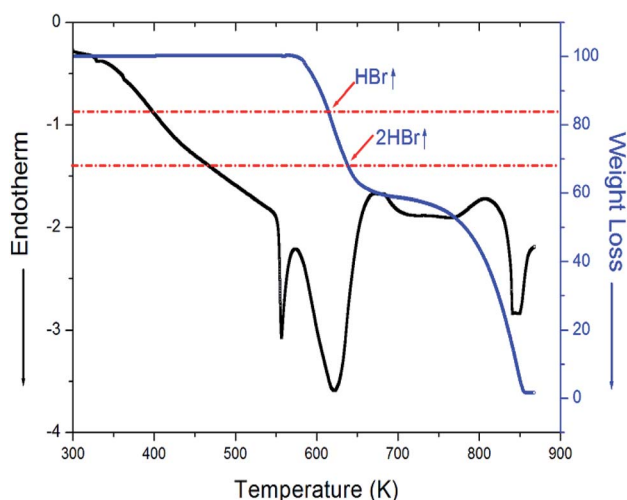


Fig. 3 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves for  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystal.

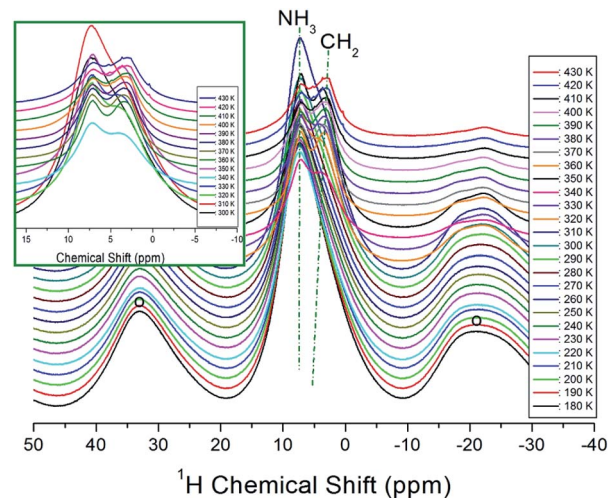


Fig. 4 *In situ*  $^1\text{H}$  MAS NMR spectra for  $\text{CH}_2$  and  $\text{NH}_3$  of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  at several temperatures. The spinning sidebands are marked with open circles (inset: expansion of  $^1\text{H}$  NMR signals above 300 K).

$\text{CdBr}_4$  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  $^1\text{H}$  NMR chemical shifts for  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  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  $^1\text{H}$  for two types of  $\text{NH}_3$  and  $\text{CH}_2$  in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$  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  $\text{NH}_3$  and  $\text{CH}_2$ , respectively. The  $^1\text{H}$  chemical shifts of  $\text{NH}_3$  indicated by dotted lines in Fig. 4 are almost independent of the temperature, while those of  $\text{CH}_2$  slightly shift toward the lower side as the temperature increases. From these results, the surrounding environment of H of  $\text{NH}_3$  does not change depending on the temperature, and that of H of  $\text{CH}_2$  changes slightly according to the temperature.

The  $^1\text{H}$  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:<sup>33–35</sup>

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

where  $I(t)$  and  $I(0)$  are the signal intensities at times  $t$  and  $t = 0$ , respectively, and  $T_{1\rho}$  denotes the spin–lattice relaxation time in the rotating frame.  $^1\text{H}$  NMR signals for  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  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



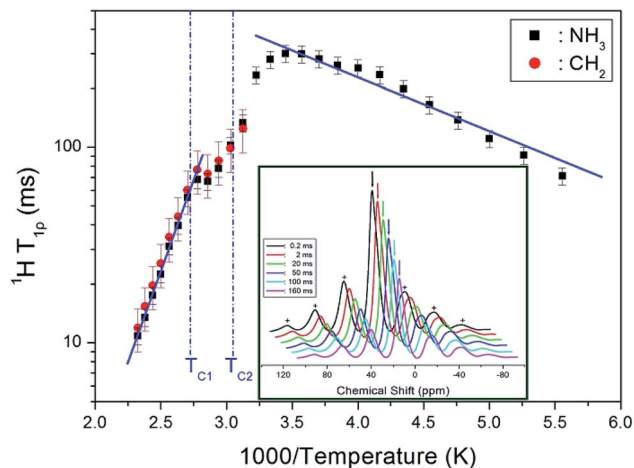


Fig. 5  $^1\text{H}$  NMR spin-lattice relaxation times  $T_{1\rho}$  of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  as a function of inverse temperature (inset: recovery curves for delay times of  $^1\text{H}$  MAS NMR spectrum in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  at 300 K).

a single exponential function shown in eqn (1). The  $T_{1\rho}$  values of the protons in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  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 ( $=T_{\text{C}2}$ ), the change in  $T_{1\rho}$  values is more or less continuous; however, at approximately 363 K ( $=T_{\text{C}1}$ ), there is a slight inflection point, marking a discontinuity. This experimental result is considered to be consistent with previously reported X-ray results,<sup>30</sup> stating that the  $c$ -value of the lattice constant is slightly shorter in the vicinity of  $T_{\text{C}2}$ , but the  $c$  value is rapidly shortened in the vicinity of  $T_{\text{C}1}$ . The  $T_{1\rho}$  values of the protons in the  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$  cation are 10–300 ms over the measured temperature range. At 180 K,  $T_{1\rho}$  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  $^1\text{H}$   $T_{1\rho}$  values for  $\text{NH}_3$  and  $\text{CH}_2$  separated from temperatures above 320 K have highly similar values. The  $T_{1\rho}$  values experience fast motion below  $T_{\text{C}2}$  and slow motion above  $T_{\text{C}2}$ . The general behavior of the  $T_{1\rho}$  for random motions of the Arrhenius type with a correlation time  $\tau_{\text{C}}$  is described in three regimes, including both fast and slow motion regimes. The fast motion regime is described as  $\omega_1\tau_{\text{C}} \ll 1$ ,  $T_{1\rho}^{-1} \propto \exp(E_{\text{a}}/k_{\text{B}}T)$ , and the slow motion regime as  $\omega_1\tau_{\text{C}} \gg 1$ ,  $T_{1\rho} \propto \omega_1^{-2} \exp(-E_{\text{a}}/k_{\text{B}}T)$ , where  $\omega_1$  denotes the radiofrequency power of the spin lock pulse, and  $E_{\text{a}}$  represents the activation energy. Different limits are satisfied for  $\omega_1\tau_{\text{C}}$  in each of the three temperature ranges, separated by  $T_{\text{C}1} = 363$  K and  $T_{\text{C}2} = 328$  K. Specifically, the limit  $\omega_1\tau_{\text{C}} \gg 1$  applies for both  $T > T_{\text{C}1}$  and  $T_{\text{C}2} < T < T_{\text{C}1}$ , and the limit  $\omega_1\tau_{\text{C}} \ll 1$  for  $T < T_{\text{C}2}$ . As indicated by the solid lines in Fig. 5,  $E_{\text{a}} = 5.21 \pm 0.38$  kJ mol $^{-1}$  at temperature below  $T_{\text{C}2}$ , while above  $T_{\text{C}1}$ ,  $E_{\text{a}} = 35.98 \pm 0.68$  kJ mol $^{-1}$ . The decrease in  $T_{1\rho}$  values with temperature indicates an increase in proton mobility at higher temperatures.

The  $^{13}\text{C}$  MAS NMR chemical shifts in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  were measured with respect to the change in temperature, as shown in Fig. 6. The  $^{13}\text{C}$  MAS NMR spectrum for TMS was obtained at 38.3 ppm at 300 K. This peak at 38.3 ppm was taken as

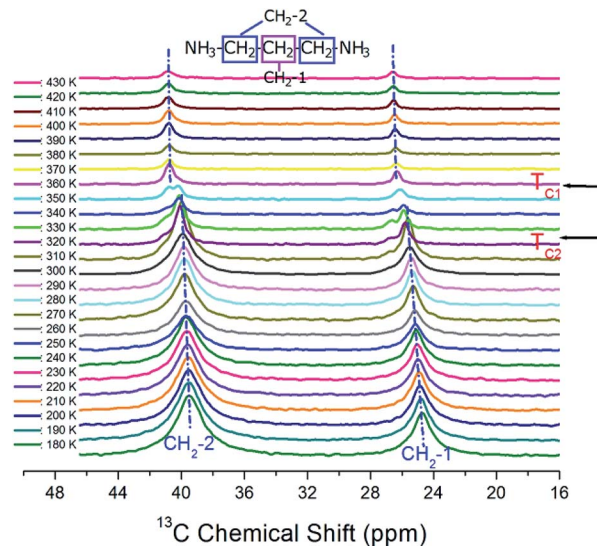


Fig. 6 *In situ*  $^{13}\text{C}$  MAS NMR spectra for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  as a function of temperature.

the standard and calibrated as a peak at zero ppm. Here, the  $\text{CH}_2$  sandwiched between two other  $\text{CH}_2$  is labeled as  $\text{CH}_2$ -1, and the  $\text{CH}_2$  close to  $\text{NH}_3$  is labeled  $\text{CH}_2$ -2. At 300 K, the carbon signals corresponding to the  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  appear at 25.55 and 39.96 ppm, respectively. Below  $T_{\text{C}2}$ ,  $^{13}\text{C}$  resonance signals show two resonance lines for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2. Between  $T_{\text{C}2}$  and  $T_{\text{C}1}$ ,  $^{13}\text{C}$  resonance signal was separated into three or four resonance lines. Their resonance lines at temperatures above  $T_{\text{C}1}$  were again reduced to two. Here, below  $T_{\text{C}2}$ , the chemical shifts of  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 are shifted slightly upward as the temperature increases, but at temperatures above  $T_{\text{C}1}$ , 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  $^{13}\text{C}$  NMR spectra with respect to the temperature is shown in

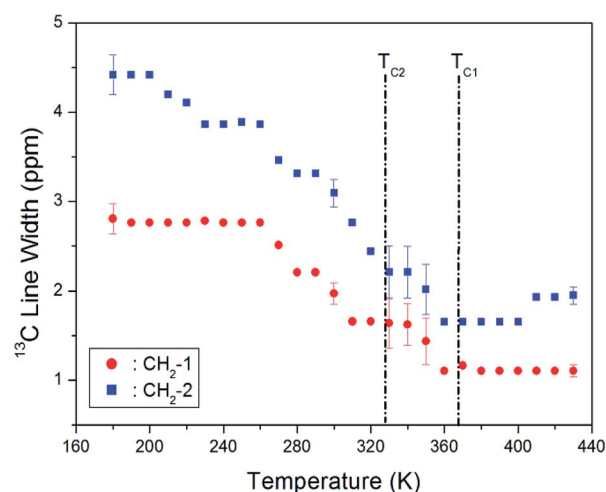


Fig. 7 Line widths of  $^{13}\text{C}$  MAS NMR signal for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  as a function of temperature.

Fig. 7. The  $^{13}\text{C}$  NMR line widths for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 decreased with an increase in temperature. The line width of the resonance line is approximately 2.8 and 4.5 ppm, respectively, for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -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  $T_{\text{C}2}$  and  $T_{\text{C}1}$ . The line width decreases with increasing temperature due to internal molecular motion, and that of  $\text{CH}_2$ -2 is broader than that of  $\text{CH}_2$ -1.

The intensities of  $^{13}\text{C}$  MAS NMR signals for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  were measured by varying the delay times at each temperature. The decay curves for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 were fitted to a single exponential equation in eqn (1).  $^{13}\text{C}$   $T_{1\rho}$  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  $^{13}\text{C}$   $T_{1\rho}$  values were obtained for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 as a function of  $1000/\text{temperature}$ , as shown in Fig. 8. The values of  $T_{1\rho}$  are somewhat continuous near  $T_{\text{C}2}$ , and discontinuous near  $T_{\text{C}1}$ . Similar to the results of  $^1\text{H}$   $T_{1\rho}$ , the discontinuous change near  $T_{\text{C}1}$  is consistent with the result of a rapid shortening of the lattice constant  $c$ -value. The  $T_{1\rho}$  vs. inverse temperature curves shows minima at 32.65 and 29.14 ms for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 at 230 K, respectively. This trend indicates that distinct molecular motions exist, where the minimum  $T_{1\rho}$  was attributed to the uniaxial rotation of  $\text{CH}_2$  ions. The  $T_{1\rho}$  values were described by the correlation time  $\tau_c$  for molecular motion. The  $T_{1\rho}$  value for the molecular motion is given by:<sup>34</sup>

$$1/T_{1\rho} = C(\gamma_C^2\gamma_H^2\hbar^2/r^6)\{4\tau_c/[1 + \omega_1^2\tau_c^2] + t_C/[1 + (\omega_H - \omega_C)^2\tau_c^2] + 3\tau_c/[1 + \omega_H^2\tau_c^2] + 6\tau_c/[1 + (\omega_H + \omega_C)^2\tau_c^2] + 6\tau_c/[1 + \omega_C^2\tau_c^2]\} \quad (2)$$

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

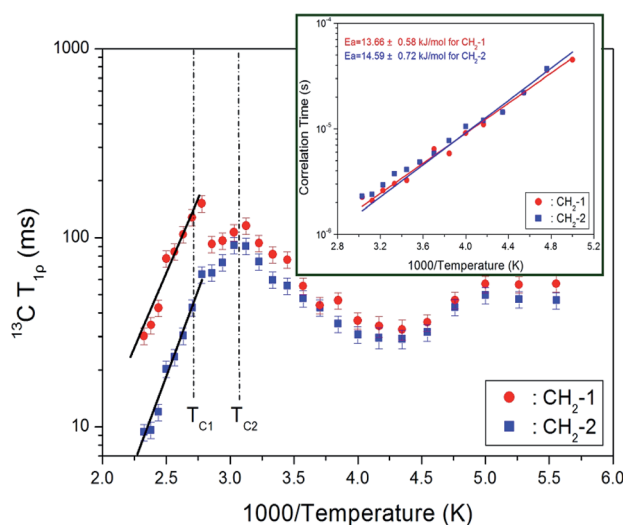


Fig. 8  $^{13}\text{C}$  NMR spin-lattice relaxation times  $T_{1\rho}$  for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  as a function of inverse temperature (inset: the correlation times for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 as a function of inverse temperature).

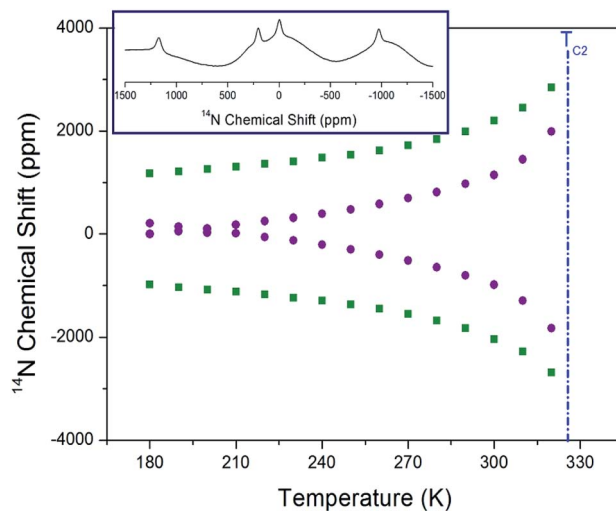


Fig. 9 Static  $^{14}\text{N}$  chemical shifts of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  single crystal as a function of temperature (inset:  $^{14}\text{N}$  chemical shift at 180 K).

distance between the proton and the carbon,  $\omega_H$  and  $\omega_C$  are the Larmor frequencies of  $^1\text{H}$  and  $^{13}\text{C}$ , respectively, and  $\omega_1$  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  $T_{1\rho}$  and  $\omega_1$ . From this coefficient, the  $\tau_c$  values can be obtained relative to the temperature. The local field fluctuation is governed by the thermal motion of  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2, which is activated by thermal energy. The  $\tau_c$  is described by Arrhenius behavior:  $\tau_c = \tau_0 \exp(-E_a/k_B T)$ , where  $\tau_0$ ,  $E_a$ , and  $k_B$  denote the pre-correlation time, activation energy of the motions, and Boltzmann constant, respectively.<sup>33</sup> As the magnitude of  $E_a$  depends on the molecular dynamics, we plotted on a logarithmic scale  $\tau_c$  vs.  $1000/\text{temperature}$  (inset of Fig. 8). Below  $T_{\text{C}2}$ ,  $E_a$  values for  $\text{CH}_2$ -1 and  $\text{CH}_2$ -2 are  $13.66 \pm 0.58$  and  $14.59 \pm 0.72$  kJ mol $^{-1}$ , respectively, and above  $T_{\text{C}1}$ ,  $E_a$  values for  $\text{CH}_2$ -1

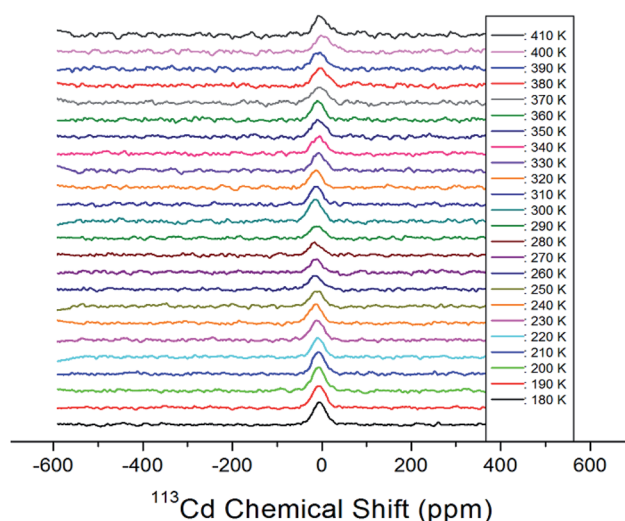


Fig. 10 Static  $^{113}\text{Cd}$  chemical shifts of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  single crystal as a function of temperature.



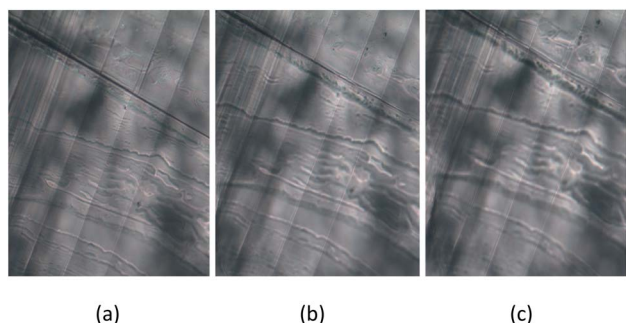


Fig. 11 Ferroelastic domain wall patterns of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystal at (a) phase III (297 K), (b) phase II (333 K), and (c) phase I (383 K).

and  $\text{CH}_2\text{-2}$  are  $30.34 \pm 3.41$  and  $35.64 \pm 2.16$   $\text{kJ mol}^{-1}$ , respectively.

Static  $^{14}\text{N}$  NMR investigations of  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  single crystal were conducted over the temperature range of 180–430 K. The  $^{14}\text{N}$  spectra obtained using the solid-state echo method by static NMR is shown in Fig. 9. Two  $^{14}\text{N}$  NMR signals were recorded from the quadrupole interactions due to the spin number  $I = 1$ . The lines with the same color below  $T_{\text{C}2}$  indicate the same pairs for  $^{14}\text{N}$ . Near 328 K ( $=T_{\text{C}2}$ ), the number of resonance lines and chemical shifts of the NMR spectrum showed abrupt changes. The changes in the  $^{14}\text{N}$  chemical shift as a function of temperature were attributed to variations in the structural geometry. The chemical shift of the  $^{14}\text{N}$  signals below  $T_{\text{C}2}$  exhibited almost continuous change, and it was difficult to observe the N signal due to the wider line width above the  $T_{\text{C}2}$  temperature. Near  $T_{\text{C}2}$ , the electric field gradient tensors at N sites varied, reflecting changes in the atomic configuration around the nitrogen atom. The environment around  $^{14}\text{N}$  in the  $\text{NH}_3$  groups indicates that the change is large near  $T_{\text{C}2}$ . Furthermore, at the temperature below  $T_{\text{C}2}$ , two different  $^{14}\text{N}$  spectra were explained as follows. According to previously

reported X-ray results,<sup>30</sup> 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  $^{113}\text{Cd}$  NMR experiments were employed to examine the structural environment in  $\text{CdBr}_6$  anions of the  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  single crystal. The spectrum exhibits only one peak due to the spin of  $I = 1/2$ .  $^{113}\text{Cd}$  NMR spectra were obtained at several temperatures, as shown in Fig. 10. The NMR chemical shift was recorded using  $\text{CdCl}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$  as the standard. At 300 K, the line width is 37.95 ppm. As shown in Fig. 10, the chemical shifts for  $^{113}\text{Cd}$  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  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  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 Aizu<sup>36</sup> and Sapriel,<sup>37</sup> 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.*,<sup>14</sup> unlike the  $mmmF2/m$  reported by Sapriel. Hence, our results support

**Table 1** Structure, space group, lattice constant ( $\text{\AA}$ ), phase transition temperature  $T_{\text{C}}$  (K), thermal decomposition temperature  $T_{\text{d}}$  (K),  $^1\text{H}$  spin–lattice relaxation time  $T_{1\rho}$  (ms),  $^{13}\text{C}$  spin–lattice relaxation time  $T_{1\rho}$  (ms), and activation energies  $E_{\text{a}}$  ( $\text{kJ mol}^{-1}$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  in  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  and  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$  crystals

	$[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$	$[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$
Structure	Orthorhombic	Orthorhombic
Space group	$Pnma$	$Pnma$
Lattice constant	$a = 7.711$ $b = 19.148$ $c = 7.856$	$a = 7.34163$ $b = 19.0300$ $c = 7.49273$
$T_{\text{C}}$	328, 363, 557	375
$T_{\text{d}}$	580	520
$^1\text{H}$ $T_{1\rho}$	280.16 ( $\text{NH}_3$ and $\text{CH}_3$ at 300 K)	411.53 ( $\text{NH}_3$ at 300 K) 551.12 ( $\text{CH}_2$ at 300 K)
$^{13}\text{C}$ $T_{1\rho}$	81.59 ( $\text{CH}_2\text{-1}$ at 300 K) 59.80 ( $\text{CH}_2\text{-2}$ at 300 K)	37.13 ( $\text{CH}_2\text{-1}$ at 300 K) 29.13 ( $\text{CH}_2\text{-2}$ at 300 K)
$^1\text{H}$ $E_{\text{a}}$	35.98 (phase I) 5.21 (phase III)	25.36 (phase I) 8.37 (phase II)
$^{13}\text{C}$ $E_{\text{a}}$ ( $\text{CH}_2\text{-1}$ )	30.34 (phase I) 13.66 (phase III)	10.18 (phase I) 29.96 (phase II)
$^{13}\text{C}$ $E_{\text{a}}$ ( $\text{CH}_2\text{-2}$ )	35.64 (phase I) 14.59 (phase III)	8.45 (phase I) 39.94 (phase II)



the mechanism of ferroelastic twin domains. Further, the two types of inequivalent  $^{14}\text{N}$  NMR lines are attributed to the ferroelastic twin domain structure.

## IV. Conclusions

We considered the physical properties of organic–inorganic hybrid perovskite  $[(\text{NH}_3)(\text{CH}_2)_3(\text{NH}_3)]\text{CdBr}_4$  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  $^1\text{H}$  NMR chemical shifts of  $\text{CH}_2$  for crystallographic environments changed more significantly with temperature than those for  $\text{NH}_3$ . At temperatures below  $T_{\text{C}2}$ , the  $^{13}\text{C}$  chemical shifts change to a slightly upward chemical shift, whereas above  $T_{\text{C}1}$ , the chemical shift hardly changes. Furthermore, the  $^{14}\text{N}$  chemical shift changes with temperature, whereas the  $^{113}\text{Cd}$  chemical shift is independent of it. This is because the environments around N change, while the  $^{113}\text{Cd}$  chemical shifts were not attributed to the rotation of  $\text{CdBr}_6$  octahedra. Finally,  $^1\text{H}$   $T_{1\rho}$  shows fast motion at low temperature and slow motion at high temperature, while  $^{13}\text{C}$   $T_{1\rho}$  shows molecular motion at low temperature and slow motion at high temperature. Shorter  $T_{1\rho}$  values at high temperature indicate that  $^1\text{H}$  and  $^{13}\text{C}$  in the organic chains are more flexible at these temperatures.

We compared the physical properties of the previously reported  $[(\text{NH}_3)(\text{CH}_2)_3(\text{NH}_3)]\text{CdCl}_4$  crystals,<sup>38</sup> and those of  $[(\text{NH}_3)(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  examined in this study. This is summarized in Table 1. The decomposition temperature of  $[(\text{NH}_3)(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  is higher than that of  $[(\text{NH}_3)(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$ . In the two compounds, the tendency of the  $^1\text{H}$  and  $^{13}\text{C}$   $T_{1\rho}$  values in terms of the temperature change is very similar, while their activation energies are very different, as shown in Table 1;  $[(\text{NH}_3)(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  has a large  $E_a$  at high temperatures, whereas  $[(\text{NH}_3)(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$  has a large  $E_a$  at low temperature. Notably, their  $^{113}\text{Cd}$  chemical shifts depend on the temperature change, which indicates the difference between the surrounding environments of  $\text{CdBr}_6$  and  $\text{CdCl}_6$  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  $T_{1\rho}$  values of the two compounds can be attributed to the differences in halogen atoms  $\text{Br}^-$  and  $\text{Cl}^-$  surrounding of Cd. These results provide insights into the molecular dynamics of the  $[(\text{NH}_3)(\text{CH}_2)_3\text{NH}_3]\text{CdBr}_4$  crystals, and are expected to facilitate their potential applications.

## Conflicts of interest

There are no conflicts to declare.

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