Structural dynamics of CH$_3$NH$_3^+$ and PbBr$_3^-$ in tetragonal and cubic phases of CH$_3$NH$_3$PbBr$_3$ hybrid perovskite by nuclear magnetic resonance

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Understanding the structural dynamics of lead-halide perovskites is essential for their advanced use as photovoltaics. Here, the structural dynamics of the CH$_3$NH$_3$ cation and PbBr$_3$ octahedra in the perovskite CH$_3$NH$_3$PbBr$_3$ were studied via nuclear magnetic resonance (NMR) to determine the mechanism of the transition from the tetragonal to cubic phase. The chemical shifts were obtained by $^1$H, $^{13}$C, and $^{207}$Pb magic angle spinning NMR and $^{14}$N static NMR. The chemical shifts of the $^1$H nuclei in CH$_3$ and NH$_3$ remained constant with increasing temperature, whereas those of the $^{13}$C and $^{207}$Pb nuclei varied near the phase transition temperature ($T_c = 236$ K), indicating that the structural environments of $^{13}$C and $^{207}$Pb change near $T_c$. The spin–lattice relaxation time $T_1$ values for $^1$H, $^{13}$C, and $^{207}$Pb nuclei increased with increasing temperature and did not exhibit an abrupt change near $T_c$. In addition, the two lines in the $^{14}$N NMR spectra superposed into one line near $T_c$, indicating the occurrence of a phase transition to a cubic phase with higher symmetry than tetragonal. Consequently, the main factor causing the phase transition from the tetragonal to cubic phase near $T_c$ is a change in the surroundings of the $^{207}$Pb nuclei in the PbBr$_3$ octahedra and of the C–N groups in the CH$_3$NH$_3$ cations.

Lead-halide perovskites currently represent the most promising photovoltaic materials for the production of low-cost, high-performance solar cells$^{1,2}$. In recent years, researchers have succeeded in significantly improving the power conversion efficiency (PCE) of this hybrid perovskite, and rapid advances in this field led to a record-high PCE. The very important for optoelectronic heterostructures are solar cells, photodetectors, and laser diodes$^{3-6}$. For this class of materials, which has the general formula CH$_3$NH$_3$Pb$^+$X$^-$(X = Cl, Br, and I), an inorganic cage of PbX$_6$ octahedra encloses an organic cation at the CH$_3$NH$_3$ site$^{7-12}$. The phase transition temperatures of CH$_3$NH$_3$PbBr$_3$, a representative perovskite, are 148.8, 154, and 236.3 K, corresponding to a total of four crystal phases$^{13-14}$, with decreasing temperature, the cubic phase (I) transforms to a tetragonal phase (II) at 236.3 K, to another tetragonal phase (III) at 154 K, and finally to an orthorhombic phase (IV) at 148.8 K. In tetragonal phase II, the CH$_3$NH$_3^+$ ions undergo isotropic reorientation, whereas in the lower-temperature phases, the reorientation of C–N axes seems to be frozen$^{15}$. All the phase transitions are first-order and order–disorder type, although the highest temperature transition is close to second-order. From the high-temperature cubic phase with freely rotating CH$_3$NH$_3$ cations, this compound enters lower-symmetry tetragonal phases and finally a low-temperature orthorhombic phase with the orientation of CH$_3$NH$_3$ cations fixed at ordered positions$^{16-20}$. At room temperature, the structure is cubic, the space group is Pm3m, and the lattice constant $a = 5.93129$ Å and $Z = 1^{13}$. In this crystal structure, there exists a CH$_3$NH$_3^+$ cation at the centre of a cube formed by corner-sharing PbBr$_6$ octahedra$^{15,21}$, as shown in Fig. 1. Below 236 K, the crystal structure has a tetragonal and belongs to the space group I4/mcm with lattice constants $a = b = 8.32$ Å, $c = 11.83$ Å, and $Z = 4^{22}$. Throughout the transition

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from the tetragonal II phase to the tetragonal III phase at 154 K, the full width at half maximum of the Raman \( \nu_6 \) band shows an abrupt increase. At lower temperatures, \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) undergoes a first-order structural phase transition from the tetragonal III (I\( _4/m\)mm) phase to the orthorhombic IV (Pnma) phase.

In a previous nuclear magnetic resonance (NMR) investigation, the temperature dependence of \(^{81}\text{Br} \) nuclear quadrupole resonance frequencies and \(^1\text{H} \) spin–lattice relaxation times in the laboratory frame \( T_1 \) for \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) were discussed by Xu et al. According to their results, the two \(^{81}\text{Br} \) NQR lines in phase II were reduced to one line in phase I. The discontinuity of the NQR line at this transition point implied a first-order transition. \(^1\text{H} \) \( T_1 \) varied continuously, and no discernible change in the free induction decay was observed during the I–II transition. The phase transition had no significant effect on the motional state of the \( \text{CH}_3\text{NH}_3^+ \) ions. Furthermore, Baikie et al. reported that the \(^1\text{H} \) magic angle spinning (MAS) NMR spectra showed two clear peaks corresponding to the \( \text{CH}_3 \) and \( \text{NH}_3 \) environments in the high-temperature phase, and the \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra of \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) showed that the \( \text{CH}_3\text{NH}_3^+ \) units undergo dynamic reorientation.

Measuring the spin–lattice relaxation time in the rotating frame \( T_{1\rho} \) by MAS NMR allows for the probing of molecular motion in the kHz range, whereas the spin–lattice relaxation time in the laboratory frame \( T_1 \) measured by static NMR reflects motion in the MHz range. Although the \(^1\text{H} \) \( T_1 \) of \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) has been examined by a few research groups, the corresponding phenomena by \(^1\text{H} \), \(^{13}\text{C} \), and \(^{207}\text{Pb} \) MAS NMR spectra and \( T_{1\rho} \) have not been fully studied. In addition, information regarding \(^{14}\text{N} \) in the \( \text{CH}_3\text{NH}_3^+ \) cation has not yet been discussed.

In the present study, the structural dynamics of the \( \text{CH}_3\text{NH}_3^+ \) cation and \( \text{PbBr}_6 \) octahedra in \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) were studied in detail by NMR to resolve the phase transition mechanisms from the tetragonal phase to the higher-temperature cubic phase. The temperature dependences of the chemical shifts and spin–lattice relaxation time in the rotating frame \( T_{1\rho} \) were measured using \(^1\text{H} \) MAS NMR, \(^{13}\text{C} \) cross-polarization (CP)/MAS NMR, and \(^{207}\text{Pb} \) MAS NMR with emphasis on the role of the \( \text{CH}_3\text{NH}_3^+ \) cation and \( \text{PbBr}_6 \) octahedra in \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \). In addition, the \(^{14}\text{N} \) static NMR spectra of \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) in the laboratory frame were acquired near the phase transition temperature. The abovementioned results help in understanding the thermal stability and the structural dynamics based on the phase transition mechanism, towards the practical application of this material.

**Experimental**

\( \text{CH}_3\text{NH}_3\text{Br} \) and \( \text{PbBr}_2 \) were dissolved in a dimethylformamide solution and heated the mixed suspension on a hot plate to obtain a transparent solution. Detailed methods for the crystal growth are given elsewhere. The \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) single crystals obtained here were orange in colour with a square shape.

Differential scanning calorimetry (DSC) (TA, DSC 25) was conducted at a heating rate of 10 °C/min over a temperature range from 190 to 525 K under nitrogen gas. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyser (TA Instrument) in an interval from 300 to 780 K at a heating rate of 10 °C/min. Approximately 11.15 mg of \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) was used in each experiment.

NMR measurements were carried out at 9.4 T using a Bruker 400 MHz Avance II + spectrometer at the Korea Basic Science Institute, Western Seoul Center. The \(^1\text{H} \), \(^{13}\text{C} \), and \(^{207}\text{Pb} \) NMR frequencies were 400.13, 100.61, and 83.75 MHz, respectively. Powdered samples were packed in zirconia MAS rotors with Macor caps, and the MAS rate was set to 10 kHz for the \(^1\text{H} \) MAS, \(^{13}\text{C} \) MAS, and \(^{207}\text{Pb} \) MAS NMR measurements to minimise spinning sideband overlap. The spin–lattice relaxation time in the rotating frame \( T_{1\rho} \) was measured using an inversion recovery pulse sequence, which employs compensating pulses. The \(^{13}\text{C} \) \( T_{1\rho} \) values were measured by varying the duration of the \(^{13}\text{C} \) spin-locking pulse applied after the CP preparation period. The width of the \( \pi/2 \) pulse used for measuring \( T_{1\rho} \) of \(^1\text{H} \) and \(^{13}\text{C} \) was 3.45 µs, and that for measuring \( T_{1\rho} \) of \(^{207}\text{Pb} \) was 3.5 µs. In addition,
14N NMR spectra of a CH3NH3PbBr3 single crystal were measured with a Larmor frequency of 28.90 MHz in the laboratory frame.

Temperature-dependent NMR spectra were recorded over 180 to 430 K; the NMR spectra and relaxation times could not be measured outside this temperature range because of the limitations of the spectrometer. Sample temperatures were held constant within ± 0.5 K by controlling the nitrogen gas flow and heating current.

Experimental results
Figure 2 shows the DSC and TGA curves obtained under a nitrogen atmosphere. DSC analysis was used to determine the phase transition temperature; only one endothermic peak related to a phase transition was observed at 236 K, which is consistent with previously reported Tc values.13,14 The thermal stability of CH3NH3PbBr3 was examined by TGA. The first occurrence of mass loss began at approximately 530 K, which represents the onset of partial thermal decomposition. The mass sharply decreased between 550 and 650 K, with a corresponding mass loss of 22% near 650 K. Optical polarizing microscopy experiments were also conducted to further understand the thermal stability at high temperatures. The colour of the crystal was orange at room temperature, as shown in the inset in Fig. 2. As the temperature increased, the state of the crystal remained the same from 400 to 500 K. Above 550 K, a slight opacity occurred at the bottom of the crystal, and at approximately 600 K, the crystal was nearly opaque.

The 1H NMR spectrum of CH3NH3PbBr3 was recorded by MAS NMR at a frequency of 400.13 MHz. Figure 3 shows the 1H MAS NMR spectrum at 300 K, where the spinning sidebands are marked with open circles and asterisks. The two peaks in the 1H spectrum correspond to CH3 and NH3 environments, with the chemical shifts at δ = 3.27 and 6.36 ppm assigned to 1H in CH3 and NH3, respectively. The chemical shifts remained quasi-constant with increasing temperature, indicating that the structural environments of 1H in the CH3 and NH3 environments remained stable.
NH3 groups were unchanged (see the Supplementary Information). Additionally, the line width (full-width at half-maximum) of the 1H MAS NMR signal at 300 K is approximately 1.62 ppm, which also remained nearly constant with temperature change.

The 1H inversion-recovery curves for both CH3 and NH3 at each temperature were fitted to exponentials to extract T1ρ. The data were well fitted a single exponential, indicating that there is one dominant relaxation mechanism acting per environment. Thus, T1ρ was determined by fitting the decay plots with the equation below\(^{26,27}\).

\[
P(t)/P_0 = \exp \left(-t/T_{1\rho}\right),
\]

where \(P(t)\) is the magnetisation, \(t\) is the spin-locking pulse duration, and \(P_0\) is the total nuclear magnetisation of 1H at thermal equilibrium. The recovery curves of 1H in CH3NH3PbBr3 were measured for various delay times at each temperature. Figure 4 (inset) shows the recovery traces for 1H measured for delay times ranging from 1 to 200 ms at 300 K. The intensity of the recovery traces differed with delay time. The T1ρ values obtained from the intensity versus delay time and shown in Fig. 4 reveal that T1ρ increased with temperature because proton hopping was accelerated. This is in agreement with Xu et al.\(^{23}\), who reported that the 1H T1 increased smoothly with increasing temperature through the high-temperature phase transition. The T1ρ values of 1H in CH3 and NH3 in the CH3NH3\(^+\) cation show similar trends with temperature and are nearly the same within the error range.

The T1ρ values show no change near the phase transition temperature (\(T_C = 236\) K). T1ρ increased with increasing temperature, reaching the maximum values of 592 ms and 456 ms for CH3 and NH3, respectively, near 330 K above the phase transition temperature, and then decreased with increasing temperature. Although the structural environment of 1H in the CH3NH3 groups does not change with temperature, their molecular motion increases at high temperatures, as indicated by the T1ρ values. Above \(T_C\), the 1H T1ρ value for CH3 slightly exceed that for NH3.

Structural analysis of the 13C and 207Pb nuclei in CH3NH3PbBr3 was performed by MAS NMR, and the corresponding spectra at 300 K are shown as insets in Fig. 5. At room temperature, the 13C and 207Pb MAS NMR spectra show one signal each at chemical shifts of \(\delta = 30.66\) and 89 ppm with respect to tetramethylsilane and PbNO3, respectively. Here, the line width for 13C at 300 K is narrow at 2.77 ppm, whereas that for 207Pb is quite broad at 206.24 ppm. Figure 5 shows the 13C and 207Pb chemical shifts of CH3NH3PbBr3 measured as a function of temperature, illustrating that the 13C and 207Pb peak positions moved to higher chemical shifts upon heating. The chemical shifts near \(T_C\) changed, in contrast to the 1H chemical shifts. The chemical shifts of the 13C and 207Pb signals relative to the reference signal are sensitive to the electronic environment of the nucleus. In particular, the 207Pb chemical shift changed more rapidly than that of 13C near \(T_C\). From these results, the phase transition from the tetragonal to cubic phase is thought to arise from a change in the PbBr6 octahedra.

To determine the T1ρ values of 13C and 207Pb in the rotating frame, the nuclear magnetisation was measured as a function of delay time. The signal intensities of the nuclear magnetisation recovery curves could be described by the single exponential function in Eq. (1), and the signal intensity followed this single exponential decay at all temperatures. From these results, the T1ρ values were obtained for 13C and 207Pb in CH3NH3PbBr3, as a function of inverse temperature, as shown in Fig. 6. The 13C and 207Pb T1ρ values for CH3 and PbBr3 seem to follow a similar trend with temperature to that of the 1H T1ρ, where the values increase with increasing temperature and are approximately continuous near \(T_C\). In addition, the 207Pb T1ρ values are much lower than 13C T1ρ.

To obtain information concerning possible changes in the surroundings of the 14N ion, static NMR spectra of 14N (I = 1) in the laboratory frame were obtained. Temperature-dependent changes in the 14N resonance frequency are attributable to alterations in the structural geometry, indicating a change in the quadrupole coupling constant of the 14N nuclei. The spectra were obtained by the solid-state echo method using static NMR at a Larmor frequency of 28.90 MHz. Two resonance signals were expected from the quadrupole interactions of the 14N nucleus with spin I = 1. The 14N NMR spectra were shown at 225 and 270 K, and the resonance frequencies referred
with respect to NH₄NO₃ as a function of temperature are shown in Fig. 7. The line widths are very narrow at all temperatures. The two resonance signals for ¹⁴N, which are attributable to NH₃, superpose into one line at the transition point of 236 K. This single ¹⁴N resonance line indicates that a phase transition takes place to a new phase with a higher symmetry than tetragonal. In tetragonal phase below T_C, the electric field gradient tensors at the N sites vary, reflecting changes in the atomic configuration around the nitrogen. But, there is no electric field gradient tensor at the ¹⁴N site in the cubic structure because of the site symmetry of m3m.

**Conclusion**

Using the information derived from NMR studies near T_C (= 236 K), we have probed the structural and dynamic features of CH₃NH₃PbBr₃ in detail and demonstrated its dynamic nature. The ionic dynamics of CH₃NH₃PbBr₃, with emphasis on the role of the CH₃NH₃ cation and PbBr₆ octahedra, were investigated by ¹H MAS NMR, ¹³C CP/MAS NMR, ²⁰⁷Pb MAS NMR, and ¹⁴N static NMR as a function of temperature. ¹H, ¹³C, and ²⁰⁷Pb NMR were used to identify the phase transition in CH₃NH₃PbBr₃ by detecting changes in the chemical shifts accompanying a change in crystallographic symmetry. Here, the CH₃ and NH₃ groups were distinguished based on the ¹H chemical shifts. The chemical shifts of the ¹H nuclei remained constant at all temperatures, whereas those of the ¹³C and ²⁰⁷Pb nuclei varied with temperature. The temperature dependence of the chemical shifts was sensitive to the rotation of the PbBr₆ octahedra. From these results, it is evident that the structural environments of ¹³C and ²⁰⁷Pb change near T_C. The change in ²⁰⁷Pb chemical shift near T_C can be explained by the rotation of PbBr₆. This is consistent with the established nature of the phase transition. Additionally, the NMR line widths of ¹H, ¹³C, and ²⁰⁷Pb were 1.62, 2.77, and 206.24 ppm, respectively, and the relaxation time is proportional to the inverse of the line width. Although the chemical shifts of ¹³C and ²⁰⁷Pb abruptly varied near T_C, the ¹H, ¹³C, and ²⁰⁷Pb T₁ values showed a similar trend with increasing temperature, and their T₁ values were continuous near T_C. These
short relaxation times indicate ease of molecular motion. The TGA results also showed that CH3NH3PbBr3 has a high thermal stability.

In addition, the abrupt change occurring in the resonance frequency of the 14N nuclei near Tc is attributable to a structural phase transition. The NH3 groups in the structure are coordinated by PbBr6, and thus atomic displacements in the environment of the 14N nuclei with temperature are correlated with PbBr6. The electrostatic interactions governed by hydrogen-bonding interactions between the NH3+ group in the CH3NH3 cation and the PbBr6 octahedra play an important role in the dynamics of the CH3NH3 cations. Consequently, the main factor causing the phase transition from the tetragonal to cubic phase near Tc is a change in the surroundings of the 207Pb nuclei in the PbBr6 octahedra and in the surroundings of C–N groups in the CH3NH3 cations. Based on these results, the structural dynamics within the CH3NH3PbBr3 perovskite structure are expected to have a significant effect on the operation mechanism of perovskite solar cells.

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Author contributions
A.R.L. designed the project and wrote the manuscript. S.H.K. performed NMR experiments. Y.L.J. suggested the idea and comment.

Competing interests
The authors declare no competing interests.

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