# Disordered Configuration of Methylammonium of $CH_3NH_3PbBr_3$ Determined by Single Crystal Neutron Diffractometry

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In order to understand the mechanism of the structural phase transition in $CH_3NH_3PbBr_3$, neutron diffraction data from the single crystal is analyzed by the least-squares method and the maximum entropy method. The disordered configuration of a methylammonium ion in a cage surrounded by eight $PbBr_6$ octahedrons is identified unambiguously. With comparing the low-temperature structure, the transition is characterized by the condensation of the rotational motion of the $PbBr_6$ octahedron around the Pb-Br axis, which accompanies the partial ordering of the methylammonium ion to reduce the site symmetry.

*Keywords:* perovskite structure; disordered configuration; methylammonium; phase transition

## 1. INTRODUCTION

An important group of ferroelectrics belongs to the perovskite structure. The general formula is $ABO_3$; the A atoms sit at the cube corners, B atoms at the body centers and the oxygens at the face centers. If the oxygen is replaced by halogen X, $ABX_3$ may also take the perovskite structure. Such examples are $CsPbX_3$ (X=Cl and Br)[1, 2]; the crystals transform from the cubic phase ($Pm3m$) to a tetragonal phase ($P4/mbm$), but no polar

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phase is reported down to low temperature.

Decades ago, the Cs ions were replaced by polar molecules $CH_3NH_3$ (abbreviated MA hereafter)[3]. The $MAPbX_3$ (X=Cl, Br and I) crystals also transformed from the cubic phase to a tetragonal phase ($I4/mcm$), which was followed by another tetragonal or orthorhombic phases. The dielectric constant increased rather high at low temperature and the orthorhombic phase was assigned to be a polar structure ($P2_1cn$)[4]. However, no ferroelectricity has been reported so far.

The calorimetric measurement indicated a large change of entropy at each phase transition in $MAPbX_3$[5]. With taking the entropy changes into account, the MA molecules were considered to take 24 configurations disorderly in the cubic phase, and the transition mechanism an order-disorder type. Three models of the successive transitions in $MAPbX_3$ were proposed[5]; the directions of the MA molecular axis referred to the cubic phase were <100>, <110> and <111> directions, for models A, B and C, respectively. The dielectric measurements indicated that the MA molecules were fully disordered in the cubic phase and were partially disordered in the tetragonal phase[6].

We have analyzed the cubic structures of $MAPbX_3$ (X=Cl, Br, I) by means of X-ray diffractometry, and concluded that the model B was most plausible among the three types of disordered configuration of MA molecules[7]. It was also demonstrated that the halogen atoms occupied four sites with equal probability in the cubic phase and became ordered in the tetragonal phase. On contradictory, the structure analysis of the tetragonal phase indicated the gradual increase of the rotation angle of $PbX_6$ octahedrons, which was a feature of a displacive transition[8,9].

X-ray investigation is difficult to represent MA directly, because Pb and X contribute dominantly than MA in the diffraction data. However, neutron scattering has an advantage of investigating MA because every atom has the same order of scattering length. Especially the protons have negative scattering length, and can be recognized definitely. So we reinvestigate the cubic perovskite structure by neutron measurement to understand the mechanism of the cubic-tetragonal transition in $MAPbBr_3$.

## 2. EXPERIMENT AND DATA ANALYSIS

Single crystals of $MAPbBr_3$ were grown as described by the previous report[3,4,5]. The crystal was transparent with orange color. A small cube of about 12mm$^3$ was mounted on a four-circle diffractometer, FONDER, installed at a beam line T2-2, JRR3M in JAERI (Tokai)[10]. Neutron diffraction intensity was collected by the use the thermal neutron whose wavelength was 1.2402Å (monochromated by Ge 311). Intensity was measured for 494 reflections in one eighth of the reciprocal space of $h$, $k$, $l<10$ with $2\theta<160^{o}$. After applying absorption and extinction corrections, we averaged equivalent reflections with $F>3\sigma(F)$, and obtained 98 independent reflections.

The space group is $Pm3m(Z=1)$ and the lattice constant is $a$=5.9305(29) Å at room temperature. Atomic parameters are refined by the use of least-squares method (BDLS) [11], with thermal parameters anisotropic for Br and isotropic for other atoms. The calculations converge to $R$=0.077, 0.065 and 0.086, for models A, B and C, respectively. Here the residual factor $R$ is defined by $R=\Sigma|F_{calc}-F_{obs}|/\Sigma|F_{obs}|$. As is expected, the model B is the best one.

As the results of the least-squares calculation, we obtain the scaled observed intensity and the estimated phase of the structure factor $F_{obs}$. All the three models give the same signs of $F_{obs}$; only two reflections 111 and 311 are negative and others are positive. Such a set of signed $F_{obs}$ is devoted to the maximum entropy method. The used program system is PRIMA[12].

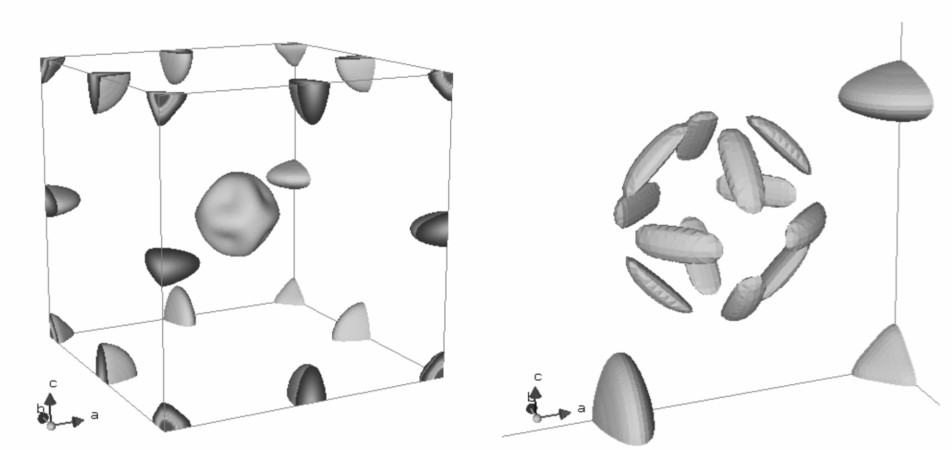


**FIGURE 1** Nuclear density of $MAPbBr_3$ of the contour surface of 3 (left). The origin is shifted by 1/2, 1/2, 1/2 from the usual $ABO_3$ structure. The right figure shows the cubic center of contour surface of 4.2 in an enlarged scale. Twelve ellipsoids represent disordered C and N.

Figure 1 shows surfaces of 3.0 nuclear density (exactly speaking, not a density but a nuclear scattering strength), drawn by a program system VENUS[13]. The Pb atoms sit at the cube corners, Br atoms at the edge centers and the MA molecules at the body centers. The disordered C-N molecule has maximums along <110> directions, which is in agreement to the model B.

At the final stage of the least-squares calculation, anisotropic thermal parameters are assigned to C and N. The calculations of the model B converge to $R$=0.0452, $wR$=0.0463, $S$=0.424 and $(\Delta/\sigma)_{max}$=0.10 for 98 reflections. The number of independent parameters is 15 with including the scale factor for $F_{obs}$.

## 3. STRUCTURE DESCRIPTION

The atomic parameters are summarized in Table I. Since the MA molecule is fully disordered, a hypothetical atom C/N with the mean scattering length is introduced to describe C and N atoms.

**Table I** Atomic coordinates and thermal parameters of $MAPbBr_3$ at RT. The estimated standard deviation is given in the parentheses.

| Atom | x | y | z | $U_{eq}$ [Å $^2$] |
|---|---|---|---|---|
| Pb | 0.0 | 0.0 | 0.0 | 0.0243( 3) |
| Br | 0.0 | 0.0 | 0.5 | 0.1020( 25) |
| C/N | 0.4134(20) | 0.4134 | 0.5 | 0.0928( 47) |
| H1 | 0.4188(38) | 0.2455(52) | 0.5 | 0.0714( 4) |
| H2 | 0.3126(28) | 0.4367(26) | 0.3568(31) | 0.0833( 4) |

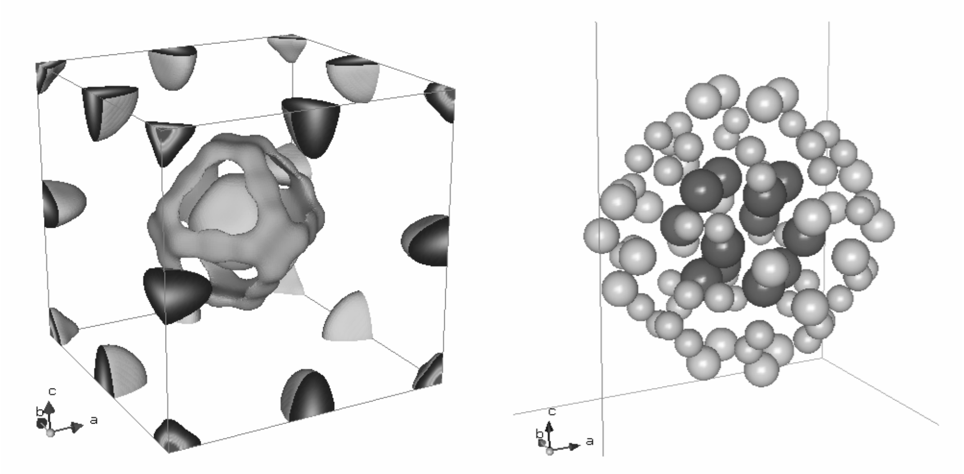
| | $U_{11}=U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{23}=U_{13}$ |
|---|---|---|---|---|
| Br | 0.1389( 51) | 0.0284( 12) | 0.0 | 0.0 |
| C/N | 0.1065( 95) | 0.0655( 47) | -0.0272( 40) | 0.0 |

The bond lengths are normal; C-N, C-H1, C-H2 are 1.45(4), 1.00(3) and 1.05(2) Å, respectively. The bond angles N-C-H1, N-C-H2 and H1-C-H2 are 133(8), 108(4) and $99(4)^{o}$, respectively. The angles are scattered a little, presumably because of an experimental error in measuring the scattering intensity.

Here we note about the large anisotropy of the thermal parameters. Since Br, C and N atoms were suspected to be in disorder, we applied the split atom method for Br, C and N. But the $R$ factor decreased little. Therefore the halogen atoms are considered to vibrate with a large amplitude, and the molecular axis of MA molecule lies just along the <110> direction.

The disordered hydrogen atoms are visualized explicitly by the contour surface of 0.8 in Fig. 2. The octahedral skeleton surrounds C and N atoms at the body center. The proton density seems to distribute continuously around the C and N atoms. The maximum positions of the proton density almost correspond to the hydrogen coordinates given in Table I. The atomic coordinates around the cubic center are shown in the right of Fig. 2

**FIGURE 2** The unit cell of MAPbBr$_3$ including hydrogen atoms. The left shows the contour surface of 0.8. The right shows a disordered methylammonium molecule, where the atomic positions are given in Table I.



## 4. DISCUSSIONS

Prior to this study, we have tried to solve the cubic structure by using the neutron reflection data from a powder sample. The Rietveld method was employed to assign each $F_{\mathrm{obs}}$ and $\sigma(F)$ from multiple reflections. Then maximum entropy method (MEM) was applied to the estimated data. But the result depended on the starting model and the convergence of the calculation was unsatisfactory. The MEM is a systematic deduction of the atomic density based on a probability consideration. The reliability and uniqueness of the given data of $F_{\mathrm{obs}}$ and $\sigma(F)$ are crucial. This is the reason why we have used the reflection data from the single crystal.

Let's discuss the structural transformation in MAPbBr$_3$. The N-C axis of a MA molecule points 12 directions of $\langle 110 \rangle_c$ in the cubic phase, while 4 directions of $[111]_t$, $[-11-1]_t$, $[-1-11]_t$ and $[1-1-1]_t$ in the tetragonal phase (*I*4/*mcm*)[8]. Since the N-C axis can take twofold rotation, equivalent 24 states and 8 states are realized in the cubic and the tetragonal phases, respectively. The entropy change of $R$ ln 3 is expected through the transition, in agreement with the experimental value of $R$ ln2.7 [5]. Thus the large entropy change can be attributed to the ordering of the MA molecules.

On the other hand, a displacive character is demonstrated around the transition, because the rotation angle of the PbBr$_6$ octahedron increases continuously with decreasing temperature[9]. In this report the abnormal distribution of Br is fully interpreted by thermal vibration, and the displacive character of the PbBr$_6$ octahedron is confirmed directly in the cubic phase.

Now which freedom, either the disordered MA molecule or the vibrating $PbBr_6$ octahedron, is the trigger of the transition? We consider that the frame of $PbBr_6$ octahedrons is so rigid that it will dominate the environment of MA molecules. The condensation of rotational motion of $PbBr_6$ octahedrons around the principal axes will induce the successive phase transition, as in the case of $CsPbX_3$[1,2]. But the freezing of the rotational modes couples with the ordering of MA molecules, which will give the large entropy change.

It has been considered that the transition temperature of displacive phase transitions increases under pressure: $dT_c/dp>0$, if zone-boundary modes freeze[14,15]. However, the phase diagram of $MAPbX_3$ has been reported as $dT_c/dp>0$[16]. The coupling between the soft rotational mode of the $PbX_6$ tetrahedrons and the disordered MA molecules may affect the pressure dependence of $T_c$.

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