Review Article

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Crystal structures of perovskite halide compounds used for solar cells

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Abstract: The crystal structures of various types of perovskite halide compounds were summarized and described. Atomic arrangements of these perovskite compounds can be investigated by X-ray diffraction and transmission electron microscopy. Based on the structural models of basic perovskite halides, X-ray and electron diffractions were calculated and compared to the experimental data. Other halides such as elemental substituted or cation ordered double perovskite compounds were also described. In addition to the ordinary 3-dimensional perovskites, low dimensional perovskites with 2-, 1-, or 0-dimensionalities were summarized. The structural stabilities of the perovskite halides could be investigated computing the tolerance and octahedral factors, which can be useful for the guideline of elemental substitution to improve the structures and properties, and several low toxic halides were proposed. For the device conformation, highly crystalline-orientated grains and dendritic structures can be formed and affected the photovoltaic properties. The actual crystal structures of perovskite halides in the thin film configuration were studied by Rietveld analysis optimizing the atomic coordinates and occupancies with low residual factors. These results are useful for structure analysis of perovskite halide crystals, which are expected to be next-generation solar cell materials.

Keywords: perovskite; crystal structure; diffraction; double perovskite; dimensionality

1 Introduction

One of the most serious problems in natural environment is global warming, which has been caused by generation of carbon dioxides (CO_{2}). Therefore, developments of new clean and efficient energy resources to suppress conventional fossil fuels such as oil, coal, and natural gas have become the very important issue to achieve Sustainable Development Goals (SDGs) proposed by United Nations. Since nuclear fusion produces high energy density and forms no CO_{2}, the various types of nuclear fusion reactors have been investigated and studies [1–5]. On the other hands, solar cells are the most promising energy device, and the merits of solar cells are as follows: 1. Use a resource that is almost infinite and free, 2. Environmentally clean, 3. No noise without moving parts, 4. Unattended operation, 5. Easy maintenance, 6. Long lifetime (~30 years), 7. Multiple use of lands [6]. However, there are several demerits such as high cost, power dependence on sunlight irradiation and small energy density. The largest barrier for spread of the solar cells is the price. Since the price for solar power generation is ~4 times more expensive compared with thermal and nuclear power generation, reducing the cost of the present silicon solar cells is mandatory. Various-type new solar cells such as poly-crystalline Si, thin film Si, CuInSe_{2}, dye-sensitized TiO_{2}, organic thin films and perovskites have been developed.

Since the first application of methylammonium lead triiodide (CH_{3}NH_{3}PbI_{3}) perovskite compound to solar cell materials [7], the perovskite solar cells have been extensively produced and studied [8–10]. These perovskite solar cells provide high photoconversion efficiencies and easy fabrication process that are comparable to organic-based solar cells [11–15]. Subsequently to achievement of conversion efficiency of ~15% [16], higher conversion efficiencies have been reported for a number of varied devices and perovskite halide crystals [17–24], and efficiencies over 20% were achieved [25–38].

The performances of photovoltaic devices are strongly dependent on the atomic structures and elemental compositions of the perovskite halide crystals [6, 39, 40]. Doping some elements such as tin (Sn) [41–45], antimony (Sb) [46–48], copper (Cu) [49–55], arsenic (As) [56], germanium (Ge) [57–59], zinc (Zn) [59–62], manganese (Mn) [63, 64], yttrium (Y) [64], strontium (Sr) [65], indium (In) [58], cobalt (Co) [58, 66], europium (Eu) [67], thallium (Tl) [58], or bismuth (Bi) [68] at the lead (Pb) site has been attempted and investigated. The photoconversion ranges of the per-
ovskite devices have been expanded by introducing Sn or Tl [41, 58].

Introducing cesium (Cs) [27, 69, 70], rubidium (Rb) [28, 71, 72], potassium (K) [37, 73, 74], sodium (Na) [75], formamidinium (HC(NH$_2$)$_2$), FA [27, 75–78], ethylammonium (CH$_3$CH$_2$NH$_3$), EA [79], or guanidinium (C(NH$_2$)$_3$), GA [80, 81] at the methylammonium (CH$_3$NH$_3$), MA site could also affect the electronic states of the perovskite halides and enhance the photoconversion efficiencies.

Numerous researches on halogen doping such as bromine (Br) [24, 27, 82, 83] or chlorine (Cl) [84–87] at the iodine (I) positions of the perovskite halide structures have been reported. Cl-doping lengthens the diffusion length, which improves the photoconversion efficiencies [15, 84–87]. Numerous studies reported that the substitutions with atom or molecule at the MA, Pb, and/or I site of the perovskite halides influence the device performances and microstructures of the photovoltaic devices.

Device performances are also dependent on the microstructures of thin film configurations, and the morphology can be controlled by additives such as poly(methyl methacrylate) [88–90], phthalocyanines [91–94], or polysilanes [95–97]. A large contact area at the TiO$_2$/perovskite interface can enhance the probability of carrier separation, which improves the short circuit current density. To reduce the grain boundaries [98], homogeneous and smooth interfaces and surfaces of the perovskite layers could improve the fill factors and open circuit voltages [99]. Improvement of hole transport layers [100–103] and electron transport layers [104–106] are also important for the carrier transport in the actual cells. In addition, it is necessary to fabricate larger the area of the cells for the commercial use [107–110].

The photovoltaic performances of the perovskite solar cells depend on the perovskite halide structures, electron transport layers, hole transport layers, nanoporous scaffold layers, and their interfacial structures. Particularly, atomic structures of the perovskite crystals have an effect upon energy gaps, conduction band minimum, valence band maximum, and carrier mobility, which should be analyzed in detail. In this review, the atomic structures of various types of perovskite halide crystals such as basic CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$), HC(NH$_2$)$_2$PbI$_3$ (FAPbI$_3$), element-substituted perovskites, low-dimensional perovskites and double perovskites, which are expected to be usable as photovoltaic device materials, are summarized and described. Because these perovskite materials often have varied nanoscopic structures for the photovoltaic devices, a summary of information on the perovskite halide crystals could be mandatory for the structural analysis and the developments of the new perovskite compounds. The nanoscopic structures of the perovskite crystals for the photovoltaic devices can be analyzed using transmission electron microscopy (TEM) and X-ray diffraction (XRD) by investigating various diffraction conditions. Although single crystal XRD is suitable for atomic structure determination, actual solar cells have thin film configurations and microcrystalline structures, and Rietveld refinements are one of the good analysis methods to determine the crystal structure of the perovskite compounds in the actual solar cell device configurations. Electron diffraction and high-resolution transmission electron microscopy are also effective instruments to analyze nanostructures of the solar cell materials [111–114] and crystal structures of the perovskite compounds [115–117].

2 X-ray diffraction and transmission electron microscopy of perovskite solar cells

To fabricate the perovskite MAPbI$_3$ and FAPbI$_3$, various methods have been developed and reported. Several representative methods to synthesize the MAPbI$_3$ compound have been studied and described [8, 106, 118–123]. Figure 1(a) is a schematic illustration of the fabricated perovskite solar cells [123]. Figure 1(b) is a photograph image of one of the examples of the actual perovskite solar cells measuring 70 mm × 70 mm, and an arrangement of Au electrodes on the substrate are observed [108].

An energy level diagram of the standard TiO$_2$/CH$_3$NH$_3$PbI$_3$ photovoltaic cells is shown in Figure 1(c). The energy levels of conduction band minimum and valence band maximum are adjusted based on the reported values [7, 124]. An energy barrier might appear at the interface between the metal and perovskite semiconductors, and the reduction of the interfacial ohmic resistances is also important [125]. Electric carriers are generated at the perovskite layer by light incidence from the transparent FTO substrate side. The TiO$_2$ layer collects emitted electrons from the CH$_3$NH$_3$PbI$_3$ compound, and the electrons are migrated to the FTO electrode. The holes are collected by the spiro-OMeTAD hole transport layer, and are migrated to Au electrodes.

Figure 2(a) is XRD patterns of standard CH$_3$NH$_3$PbI$_3$ thin films on the glass substrate before and after heating [123]. The diffraction reflections in Figure 2 are indexed by tetragonal and cubic structures for the as-prepared and heated films, respectively. Although only diffraction
peaks due to the perovskite halide phase are observed for the as-deposited film, a wider diffraction peak owing to PbI$_2$ formation by heating is observed, as shown in Figure 2(a). A small amount of PbI$_2$ sometimes contribute to the improvement of the photovoltaic properties [126–133], which would have roles of electron-blocking and protecting the perovskite phase against the air at the surface of the perovskite layer. Figure 2(b) and Figure 2(c) are enlarged XRD profiles of Figure 2(a). Split diffraction reflections of 002+110 and 004+220 for the as-prepared specimen varied to 100 and 200 reflections after heating, which shows a structure transformation from the tetragonal to cubic symmetry. The standard CH$_3$NH$_3$PbI$_3$ perovskite crystals provide structurally transition from the tetragonal to cubic structure at ~330 K [134–136], as described in detail in the later section.

The XRD profiles in Figure 2 indicate the structural transformation of the CH$_3$NH$_3$PbI$_3$ compound and the partial desorption of CH$_3$NH$_3^+$ to form PbI$_2$ during annealing. It should be careful that the structural transformation pre-
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Presented here could be different from the isolated single crystals, and the nanocrystals of perovskite halides with cubic symmetry might be “frozen” both in and on the mesoporous TiO$_2$ layers, as indicated in Figure 1(a). A very weak reflection corresponding to 211 of the tetragonal symmetry might appear at the left side of the cubic 111 reflection for the annealed CH$_3$NH$_3$PbI$_3$, as observed in Figure 2(a). To be accurate, it might be better to refer to the cubic phase as a “pseudo-cubic” phase. The pseudo-cubic defined here is a crystal structure that has nearly cubic symmetry with a/c of ~1, and a weak 211 reflection of the tetragonal symmetry appears at ~23.5° by violation of extinction rule of the cubic symmetry.

If amounts of the specimen are very small, it is hard to acquire the enough XRD intensity from the small specimen. Since a small amount of the sample is enough for transmission electron microscopy, the TEM analysis is one of the most powerful methods to acquire the 3-dimensional atomic arrangement directly. By taking electron diffraction patterns along several crystal directions, fundamental structural information such as lattice constants and crystal systems can be obtained. Many of the perovskite halide compounds have analogous atomic arrangements to the known perovskite compounds, and the atomic arrangement can be evaluated from the database on the known structures. For instance, various new crystal structures of lots of novel superconducting perovskite copper oxides have been identified by the TEM observation [117]. The atomic arrangements of the perovskite structures have been roughly determined from the electron diffraction patterns, structural images, and elemental analysis by energy dispersive X-ray spectroscopy [115–117].

A TEM image of the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface that is an orthodox device structure of the perovskite solar cell, is shown in Figures 3(a) [123]. In addition to many TiO$_2$ particles with sizes of ~50 nm, the CH$_3$NH$_3$PbI$_3$ grain with dark contrast is observed in this TEM image. Figure 3(b) is a selected area electron diffraction pattern of Figure 3(a). Several Debye–Scherrer rings due to the anatase TiO$_2$ nanoparticles are observed, as indicated by white arrows. In addition to the Debye–Scherrer rings, diffraction reflections due to cubic CH$_3$NH$_3$PbI$_3$ crystals are also observed as indicated by blue arrows and a rectangle.

Figure 3(c) is a high-resolution structural image of the CH$_3$NH$_3$PbI$_3$ recorded parallel to the [001] direction. Dark dots indicating Pb sites are clearly recognized in the image, and iodine sites also show slight contrast between the Pb atoms along the [100] and [010] directions of the CH$_3$NH$_3$PbI$_3$ crystal. CH$_3$NH$_3$ ions are not recognized as clear dark dots owing to the small atomic number of C, N, and H.

Figure 3: (a) TEM image and (b) electron diffraction pattern of TiO$_2$/CH$_3$NH$_3$PbI$_3$. “P” in the diffraction pattern indicates CH$_3$NH$_3$PbI$_3$ perovskite phase. Copyright (2014) The Japan Society of Applied Physics. (c) High-resolution TEM image of CH$_3$NH$_3$PbI$_3$. © 2014 DE GRUYTER.
3 Estimation of structural stability by tolerance factors

The perovskite structures used for solar cell devices often have a chemical composition of ABX$_3$, where A is generally a monovalent cation, B is a divalent cation, and X is a monovalent halogen anion. A basic structural model of ABX$_3$ perovskite is shown in Figure 4, and the B cation forms BX$_6$ octahedron. For the CH$_3$NH$_3$PbI$_3$ crystal, $A^+$ is CH$_3$NH$_3^+$, $B^{2+}$ is Pb$^{2+}$, and $X^-$ is I$^-$. For actual application for solar cells, the basic CH$_3$NH$_3$PbI$_3$ perovskite compounds have two major problems, the toxicity of Pb and the lack of durability. The MAPbI$_3$ compounds are generally unstable at room temperature in air, and improvement of the stability is one of the most significant issues [126, 137–140]. One approach to stabilize the MAPbI$_3$ is to introduce several elements to the perovskite halide structures. Regarding to the toxicity of Pb, elemental substitution at the Pb sites in the MAPbI$_3$ compounds is one of the solutions.

To estimate the structural stability of these perovskite halide materials, an indicator called tolerance factor ($t$) has been computed and used [141–144]. This tolerance factor is calculated as follows:

$$ t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}} $$

where $r_A$, $r_B$, and $r_X$ are the ionic radii of the A, B, and X ions, respectively, in the ABX$_3$ perovskite halide compounds. The ionic radii of elements constituting ABX$_3$ perovskites are summarized and shown in Figure 4 [8, 145, 146], where the coordination numbers of A, B, and X ions are 12, 6, and 6, respectively. In addition, the ionic radii of CH$_3$NH$_3^+$ (MA$^+$), HC(NH$_2$)$_2$ (FA$^+$), CH$_3$CH$_2$NH$_2$ (EA$^+$), and C(NH$_2$)$_2$ (GA$^+$) are 2.17, 2.53, 2.74, and 2.78 Å, respectively [147]. When the $t$-value is 1, the perovskite compound has a stable crystal structure with cubic symmetry. Another approach to estimate the structural stabilities of the perovskite is to examine the octahedral factor [142, 143, 148]. The octahedral factor ($\mu$) can be expressed as

$$ \mu = \frac{r_B}{r_X} $$

The $t$- and $\mu$-factors are experiential guidelines that do not consider the ionic interactions in the perovskite crystal. Thus, stability ranges of the ABX$_3$ perovskite halides change being affected by the elemental and ionic properties. Based on the many previous studies on halide perovskites, the perovskite structure could be experientially formed in the range of $0.813 \leq t \leq 1.107$ and $0.442 \leq \mu \leq 0.895$ [146]. When $\mu$ increases from 0.414 to 0.592, 7-coordinated octahedra would be more suitable [149], and $\mu$ values below 0.592 would be better to stabilize the BX$_6$ octahedra.

![Figure 4: Structural model of ABX$_3$ perovskite and ionic radii (Å) of elements and molecules.](image-url)
The $t$- and $\mu$-factors of the ABX$_3$ perovskite halide compounds using elements and molecules in Figure 4 were calculated and summarized, as shown in Figure 5. The $t$-factor of MAPbI$_3$ is calculated to be 0.912, which indicates the MAPbI$_3$ may be somewhat unstable. One approach to stabilize the perovskite structure is to substitute organic ions or other elements in the MAPbI$_3$ crystal. The octahedral factor of MAPbI$_3$ is fixed at 0.541, which is within the range of the perovskite formation. The $t$- and $\mu$-factors of FAPbI$_3$ are 0.987 and 0.541, respectively, which indicates that the FAPbI$_3$ crystal would be more stable than MAPbI$_3$. The $t$- and $\mu$-values of the other compounds are summarized and listed in Table 1 and ref. [144]. Possible compositions ($0.813 \leq t \leq 1.107, 0.442 \leq \mu \leq 0.541$) for the perovskite structures were indicated in bold fonts in Table 1, and candidates of low-toxicity perovskite compounds are indicated by green color.

The $t$- and $\mu$-factors can be computed by assuming that ions have rigid spheres and that the ionic radii are constant. However, the $t$- and $\mu$-factors are a simple and helpful guideline to estimate the structural stability of the perovskite halides, and a new tolerance factor was also proposed [150]. First-principles calculations based on density functional theory also represent a powerful method to predict the stability and properties of the crystals and doped clusters [151–154].

4 Crystal structures of CH$_3$NH$_3$PbI$_3$

CH$_3$NH$_3$PbI$_3$ is the most standard and widely used compounds for perovskite solar cells. Although the crystal structure of the CH$_3$NH$_3$PbI$_3$ has been investigated in detail, there are still some vague regions, and several structural models are proposed.

The CH$_3$NH$_3$PbI$_3$ crystals have perovskite-type crystal structures and show structural transitions upon heating [155–157]. The transition temperatures and crystal systems are listed in Table 2. As the temperature decreases to ~330 K, the cubic phase is transformed into the tetragonal phase [158] and then converted to the orthorhombic phase at ~160 K [118]. This transition temperature of ~330 K is nearly room temperature, which may also cause the structural instability.
Table 3: Crystal systems and transition temperatures of CH$_3$NH$_3$PbI$_3$.

| Compound   | $t$   | $\mu$ | Compound   | $t$   | $\mu$ | Compound   | $t$   | $\mu$ | Compound   | $t$   | $\mu$ |
|------------|-------|-------|------------|-------|-------|------------|-------|-------|------------|-------|-------|
| RbHgCl     | 0.826 | 0.607 | CsHgBr     | 0.826 | 0.607 | MAPbI$_3$  | 0.912 | 0.541 | FAPbI$_3$  | 0.987 | 0.541 |
| RbHgBr     | 0.920 | 0.541 | CsHgI      | 0.920 | 0.541 | MAPbBr$_3$ | 1.091 | 0.541 | FAPbBr$_3$ | 1.091 | 0.541 |
| RbHgI      | 0.941 | 0.541 | CsHgCl     | 0.941 | 0.541 | MAPbCl$_3$ | 1.120 | 0.541 | FAPbCl$_3$ | 1.120 | 0.541 |
| RbHg       | 0.941 | 0.541 | CsHg       | 0.941 | 0.541 | MAPb      | 1.120 | 0.541 | FAPb      | 1.120 | 0.541 |
| RbBr       | 0.941 | 0.541 | CsCl       | 0.941 | 0.541 | MAPbCl$_3$ | 1.120 | 0.541 | FAPbCl$_3$ | 1.120 | 0.541 |
| RbI        | 0.941 | 0.541 | Cs         | 0.941 | 0.541 | MAPb      | 1.120 | 0.541 | FAPb      | 1.120 | 0.541 |

Table 2: Crystal systems and transition temperatures of CH$_3$NH$_3$PbI$_3$.

| Reference | T (K) | T (K) | T (K) | T (K) |
|-----------|-------|-------|-------|-------|
| Cubic (a) | 1.059 | 1.059 | 1.059 | 1.059 |
| Cubic (a) | 1.059 | 1.059 | 1.059 | 1.059 |
| Cubic (a) | 1.059 | 1.059 | 1.059 | 1.059 |

Detailed crystal systems and lattice constants of CH$_3$NH$_3$PbI$_3$ are summarized and listed in Table 3. Several structural models as the $\alpha$-CH$_3$NH$_3$PbI$_3$ phase have been reported, as listed in Table 3 and Figure 6. The structural models presented here are drawn with VESTA [162]. For the model in Figure 6(a), the methyl ammonium (MA)
As described in section 2, the pseudo-cubic has nearly cubic two structural configurations on the C₂ axis. Accordingly, the degrees of freedom of the MA⁺ ions could be disordered with regard to the orientation of the C-N axis itself and around the C-N axis. Coexistence of the cubic and tetragonal phases was also observed over a range of temperature, which may indicate a predicted tricritical phase transition [136].

Along with the arrangement of the CH₃NH₃⁺, the displacement of iodine ion (I⁻) perpendicular to the crystal axis is observed, as shown in Figure 6(a). Site occupancies of C, N, and I were determined to be 1/12, 1/12 and 1/4, respectively.

Although some amounts of point defects such as CH₃NH₃ and deviations of stoichiometry could exist at the crystal surface even for the single crystal of CH₃NH₃PbI₃, the electronic charge deviation may be compensated by introducing the iodine defects or deviations of the mixed cation valences of Pb²⁺ and Pb₄⁺, and charge neutral conditions could be maintained electronically. This kind of tolerance for defects and nonstoichiometry would provide a wide processing window for these perovskite halide thin film crystals with good electronic properties.

| Structure type | Crystal system | Space group | Lattice constant (Å) | V (Å³) | Z | V/Z (Å³) | Analysis method | Temperature (K) | Reference |
|----------------|----------------|-------------|----------------------|--------|----|----------|----------------|----------------|-----------|
| α              | Cubic          | Pm3m       | a = 6.315(3)         | 251.8  | 1  | 251.8    | SCND            | 350            | 159       |
| α              | Cubic          | Pm3m       | a = 6.31728(27)      | 252.1  | 1  | 252.1    | NPD             | 352            | 160       |
| α              | Cubic          | Pm3m       | a = 6.391(1)         | 261.0  | 1  | 261.0    | SCXRD           | 338            | 134       |
| α              | Tetragonal     | P4mm       | a = 6.3115(2),       | 251.6  | 1  | 251.6    | SCXRD           | 400            | 161       |
| γ              | Orthorhombic   | Pnma       | a = 8.8796(6),       | 995.6  | 4  | 248.9    | SCND            | 295            | 159       |
| γ              | Orthorhombic   | Pnma       | a = 8.8349(2),       | 990.0  | 4  | 247.5    | SCXRD           | 293            | 161       |
| γ              | Orthorhombic   | Pnma       | a = 8.80623(18),     | 982.3  | 4  | 245.6    | SCXRD           | 220            | 158       |
| γ              | Orthorhombic   | Pnma       | a = 8.78612(9),      | 985.9  | 4  | 246.5    | NPD             | 180            | 160       |
| γ              | Orthorhombic   | Pnma       | a = 8.86574(30),     | 960.3  | 4  | 240.0    | NPD             | 100            | 160       |
| γ              | Orthorhombic   | Pnma       | a = 8.85362(11),     | 951.0  | 4  | 237.8    | SCXRD           | 100            | 118       |
| γ              | Orthorhombic   | Pnma       | a = 8.8155(4),       | 951.1  | 4  | 237.8    | NPD             | 4              | 135       |
For the model in Figure 6(b), the lattice is almost pseudo-cubic, and the C–N arrangement is ordered along the [001] direction [161]. On the other hand, the N atom was assumed to be the same as the C atom for the model in Figure 6(c) [160].

Detailed structure analysis including the hydrogen atom positions of the CH$_3$NH$_3$PbI$_3$ was carried out for a single crystal using neutron diffraction [159], and the detailed structural model based on the determined atomic positions (Table 4) is shown in Figure 6(d). Local structural models of CH$_3$NH$_3^+$ in the MAPbI$_3$ crystal aligned along three different main directions ([100], [110], and [111]) were determined, as shown in Figure 7. The measured site occupancy ratios of the CH$_3$NH$_3^+$ cations for the [110], [100], and [111] directions were 0.670:0.187:0.143 [159], respectively, which indicates that the CH$_3$NH$_3^+$ cations reside primarily along the [110] direction of the cubic MAPbI$_3$ crystal. This result agrees well with the reported calculations of the CH$_3$NH$_3^+$ arrangement by density functional theory (DFT) [163]. Atomic displacement parameter (ADP) ellipsoids shown at 50% probability of the MAPbI$_3$ model in Figure 6(d) are shown in Figure 6(e). Large displacements of iodine ions in the crystal are observed, as also shown in the model in Figure 6(a). The large thermal ellipsoids for the iodine ions indicate that the actual atomic positions of the iodine may deviate from the ideal 3-dimensional Wyckhoff position [159].

At room temperature around 300 K, a tetragonal structure is formed, as shown in Figure 8 and Table 5 [159]. In the tetragonal CH$_3$NH$_3$PbI$_3$ crystal, I$^-$ positions are almost fixed, which results in the lowered crystal symmetry compared with the cubic structure. Occupancies of C, N, and H were set as 1/8 for the MAPbI$_3$ with a tetragonal structure. The NH$_3^+$ cation is disordered in 4 different positions and located around the adjacent I$^-$ of the PbI$_6$ octahedron [159]. Conversely, the CH$_3$ is located at 8 different positions around the body positions of the unit cell. For both tetragonal and cubic MAPbI$_3$ structures, the central points of the C–N bond are located off-center of the unit cell. This is caused by the hydrogen bond-like interactions between the NH$_3^+$ and the I$^-$ ions of the PbI$_6$ octahedron in the perovskite crystal [159].
### Table 4: Structural parameters of cubic CH₃NH₃PbI₃. For space group Pm̅3m (221), a = 6.315(3) Å at 350 K. $U_{eq}$ is equivalent isotropic displacement parameters. Reproduced with permission [159]. Copyright 2016, American Chemical Society.

| Atom | Wyckoff site | x    | y    | z    | Occupancy | $U_{eq}$ (Å²) |
|------|--------------|------|------|------|-----------|---------------|
| Pb1  | 1a           | 0    | 0    | 0    | 1.0       | 0.0301(3)     |
| I1   | 3d           | 0    | 0    | 0.5  | 1.0       | 0.1219(1)     |
| C1   | 12j          | 0.5  | 0.4402(9) | 0.4402(9) | 0.01397(1) | 0.076(5)      |
| H1A  | 48n          | 0.6032 | 0.4854 | 0.3158 | 0.01397(1) | 0.092(5)      |
| H1B  | 48n          | 0.3445 | 0.4214 | 0.3798 | 0.01397(1) | 0.092(5)      |
| H1C  | 48n          | 0.5523 | 0.2950 | 0.5062 | 0.01397(1) | 0.092(5)      |
| N1   | 12j          | 0.5  | 0.6054(9) | 0.6054(9) | 0.01397(1) | 0.099(5)      |
| H3D  | 48n          | 0.4712 | 0.7506 | 0.5370 | 0.01397(1) | 0.092(5)      |
| H3E  | 48n          | 0.6452 | 0.6081 | 0.6795 | 0.01397(1) | 0.092(5)      |
| H3F  | 48n          | 0.3836 | 0.5727 | 0.7149 | 0.01397(1) | 0.092(5)      |
| C2   | 6f           | 0.420(2) | 0.5  | 0.5  | 0.003886  | 0.076(5)      |
| H2A  | 48n          | 0.3636 | 0.5759 | 0.6389 | 0.003886  | 0.092(5)      |
| H2B  | 48n          | 0.3636 | 0.3418 | 0.4963 | 0.003886  | 0.092(5)      |
| H2C  | 48n          | 0.3636 | 0.5823 | 0.3648 | 0.003886  | 0.092(5)      |
| N2   | 6f           | 0.653(2) | 0.5000 | 0.5  | 0.003886  | 0.099(5)      |
| H2D  | 48n          | 0.7069 | 0.4187 | 0.6305 | 0.003886  | 0.092(5)      |
| H2E  | 48n          | 0.7069 | 0.6537 | 0.5052 | 0.003886  | 0.092(5)      |
| H2F  | 48n          | 0.7069 | 0.4277 | 0.3643 | 0.003886  | 0.092(5)      |
| C3   | 8g           | 0.4544(13) | 0.4544(13) | 0.4544(13) | 0.00297(1) | 0.076(5)      |
| H3A  | 48n          | 0.3808 | 0.3367 | 0.5488 | 0.00297(1) | 0.092(5)      |
| H3B  | 48n          | 0.5488 | 0.3808 | 0.3367 | 0.00297(1) | 0.092(5)      |
| H3C  | 48n          | 0.3367 | 0.5488 | 0.3808 | 0.00297(1) | 0.092(5)      |
| N3   | 8g           | 0.5890(13) | 0.5890(13) | 0.5890(13) | 0.00297(1) | 0.099(5)      |
| H3D  | 48n          | 0.7171 | 0.5027 | 0.6414 | 0.00297(1) | 0.092(5)      |
| H3E  | 48n          | 0.5027 | 0.6414 | 0.7171 | 0.00297(1) | 0.092(5)      |
| H3F  | 48n          | 0.6414 | 0.7171 | 0.5027 | 0.00297(1) | 0.092(5)      |

### Table 5: Structural parameters of tetragonal CH₃NH₃PbI₃. For space group I4/mcm (140), a = 8.8796(6), c = 12.6266(18) Å at 295 K. $U_{eq}$ is equivalent isotropic displacement parameters. Reproduced with permission [159]. Copyright 2016, American Chemical Society.

| Atom | Wyckoff site | x    | y    | z    | Occupancy | $U_{eq}$ (Å²) |
|------|--------------|------|------|------|-----------|---------------|
| Pb   | 4c           | 0.5  | 0.5  | 0.5  | 1.0       | 0.0262(4)     |
| I1   | 4a           | 0.5  | 0.5  | 0.75 | 1.0       | 0.069(2)      |
| I2   | 8h           | 0.7868(4) | 0.2868(4) | 0.5  | 1.0       | 0.0686(15)    |
| C    | 32m          | −0.0466(19) | 0.527(2) | 0.2385(15) | 0.125 | 0.090(4)    |
| H1   | 32m          | −0.0757 | 0.6133 | 0.2925 | 0.125 | 0.104(8)    |
| H2   | 32m          | −0.1433 | 0.4610 | 0.2213 | 0.125 | 0.096(7)    |
| H3   | 32m          | −0.0049 | 0.5750 | 0.1676 | 0.125 | 0.109(8)    |
| N    | 32m          | 0.0696(8) | 0.4304(8) | 0.2858(10) | 0.125 | 0.085(3)    |
| H4   | 32m          | 0.1649 | 0.4934 | 0.3000 | 0.125 | 0.103(7)    |
| H5   | 32m          | 0.0952 | 0.3439 | 0.2345 | 0.125 | 0.097(7)    |
| H6   | 32m          | 0.0304 | 0.3864 | 0.3560 | 0.125 | 0.092(7)    |
Figure 7: Local structural models of cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$. $\text{CH}_3\text{NH}_3$ ions are set along the (a) [100], (b) [110], and (c) [111] directions.

Figure 8: Structural models of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ observed along (a) [010], (b) [110], and (c) [001] directions. (d) Perspective view of the tetragonal structure and (e) atomic displacement parameter ellipsoids shown at 50% probability of (d).
Figure 9: Structural models of orthorhombic CH$_3$NH$_3$PbI$_3$ observed along (a) [001], (b) [110], and (c) [010] directions. (d) Perspective view of the orthorhombic structure.

When the temperature falls below 160 K, the tetragonal CH$_3$NH$_3$PbI$_3$ structure transforms into the orthorhombic CH$_3$NH$_3$PbI$_3$ structure, which is caused by the molecular ordering of the CH$_3$NH$_3^+$, as observed in Figure 9. All hydrogen positions in the MAPbI$_3$ were determined, as indicated in the figures. Energy band gaps of the CH$_3$NH$_3$PbI$_3$ perovskite were also computed and measured [118]. The energy gap widens with lowering temperature from the first principle calculation, and the energy gaps were measured to be $\sim$1.5 eV, which is close to the adequate energy gap value as that of solar cell materials.

Both microstructures and crystal structures of the perovskite halide compounds can be investigated using XRD. The measured XRD results indicate whether the specimen is single phase or mixed phases with other compounds. If the specimen is composed of nanoscale grains, the crystallite size parallel to the substrate can be calculated from the full width at half maximum (FWHM) of the diffraction angle. Using the XRD information, analyses of electron diffraction patterns and high-resolution TEM structural images will be easier. If the specimen has a known and reported structure, Miller indices and the plane distances (d) can be estimated from the XRD reflections. If the specimen is a completely unknown material, the d values can be calculated using XRD data, which can facilitate the structural analysis.

Calculated XRD profiles of the cubic, tetragonal, and orthorhombic CH$_3$NH$_3$PbI$_3$ are shown in Figure 10, and the Miller indices, diffraction angles, d-spacings, and relative intensities of the CH$_3$NH$_3$PbI$_3$ with cubic and tetragonal structures are summarized and listed in Tables 6 and 7, respectively. Asterisks in the tetragonal phase indicate the 211 and 213 diffraction reflections, which are inconsistent with cubic symmetry and helpful in distinguishing between the cubic and tetragonal symmetry of the CH$_3$NH$_3$PbI$_3$ crystal.

Calculated XRD patterns of tetragonal CH$_3$NH$_3$PbI$_3$ with four FWHM values are shown in Figure 11. As the crystallite size becomes smaller, the FWHM value increases, and the reflection intensities change as shown in Figure 11(a). Figure 11(b) displays enlarged XRD profiles for the tetragonal CH$_3$NH$_3$PbI$_3$. As the FWHM values increase, the 004 and 220 reflections for a tetragonal symmetry appear to be combined into the one 220 peak, which corresponds to the 200 peak of a cubic symmetry. This com-
Table 6: Calculated X-ray diffraction parameters of cubic CH$_3$NH$_3$PbI$_3$. Equivalent indices were combined. For space group Pm$ar{3}$m (221), $a = 6.315(3)$ Å at 350 K.

| Index | $2\theta$ (°) | d-spacing (Å) | Relative intensity (%) | Multiplicity |
|-------|---------------|---------------|------------------------|--------------|
| 110   | 16.40124      | 6.3150        | 100                    | 6            |
| 110   | 19.8665       | 4.4654        | 8                      | 12           |
| 111   | 24.3935       | 3.6460        | 6                      | 8            |
| 200   | 28.2399       | 3.1575        | 50                     | 6            |
| 210   | 31.6557       | 2.8242        | 48                     | 24           |
| 211   | 34.7687       | 2.5781        | 5                      | 24           |
| 220   | 40.3638       | 2.2327        | 27                     | 12           |
| 221   | 42.9296       | 2.1050        | 17                     | 24           |
| 300   | 42.9296       | 2.1050        | 4                      | 6            |
| 310   | 45.3773       | 1.9970        | 3                      | 24           |
| 311   | 47.7259       | 1.9040        | 1                      | 24           |
| 222   | 49.9899       | 1.8230        | 7                      | 8            |
| 320   | 52.1812       | 1.7515        | 8                      | 24           |
| 321   | 54.3093       | 1.6878        | 3                      | 48           |
| 400   | 58.4060       | 1.5788        | 3                      | 6            |

Figure 11: (a) Calculated X-ray diffraction patterns of tetragonal CH$_3$NH$_3$PbI$_3$ with various FWHM values. (b) Enlarged diffraction patterns of (a).

Table 7: Calculated X-ray diffraction parameters of tetragonal CH$_3$NH$_3$PbI$_3$. Equivalent indices were combined. For space group I4/mcm (140), $a = 8.8796(6)$, $c = 12.6266(18)$ Å at 295 K.

| Index | $2\theta$ (°) | d-spacing (Å) | Relative intensity (%) | Multiplicity |
|-------|---------------|---------------|------------------------|--------------|
| 002   | 14.0162       | 6.3133        | 53                     | 2            |
| 110   | 14.0935       | 6.2788        | 100                    | 4            |
| 112   | 19.9271       | 4.4519        | 7                      | 8            |
| 200   | 19.9821       | 4.4398        | 7                      | 4            |
| 211   | 23.4646       | 3.7881        | 15                     | 16           |
| 202   | 24.4909       | 3.6317        | 12                     | 8            |
| 004   | 28.2477       | 3.1567        | 33                     | 2            |
| 220   | 28.4060       | 3.1394        | 54                     | 4            |
| 213   | 30.9339       | 2.8884        | 6                      | 16           |
| 114   | 31.7002       | 2.8203        | 29                     | 8            |
| 222   | 31.8072       | 2.8110        | 22                     | 8            |
| 310   | 31.8429       | 2.8080        | 35                     | 8            |
| 204   | 34.8441       | 2.5727        | 4                      | 8            |
| 312   | 34.9427       | 2.5656        | 8                      | 16           |
| 321   | 37.1645       | 2.4172        | 2                      | 16           |
| 224   | 40.4910       | 2.2260        | 34                     | 8            |
| 400   | 40.6065       | 2.2199        | 13                     | 4            |
| 215   | 42.3817       | 2.1309        | 2                      | 16           |
| 323   | 42.4930       | 2.1256        | 1                      | 16           |
| 411   | 42.5486       | 2.1230        | 7                      | 16           |
| 006   | 42.9417       | 2.1044        | 2                      | 2            |
| 314   | 43.0794       | 2.0980        | 27                     | 16           |
| 402   | 43.1618       | 2.0942        | 7                      | 8            |
| 330   | 43.1893       | 2.0929        | 2                      | 4            |
| 420   | 45.6535       | 1.9855        | 3                      | 8            |
| 413   | 47.378        | 1.9172        | 4                      | 16           |
| 404   | 50.2002       | 1.8158        | 12                     | 8            |
| 325   | 51.8101       | 1.7631        | 1                      | 16           |
| 431   | 51.9534       | 1.7586        | 2                      | 16           |
| 226   | 52.2914       | 1.7480        | 3                      | 8            |
| 334   | 52.4100       | 1.7444        | 3                      | 8            |
| 510   | 52.5048       | 1.7414        | 4                      | 8            |
| 316   | 54.4407       | 1.6840        | 2                      | 16           |
| 424   | 54.5560       | 1.6807        | 4                      | 8            |
| 512   | 54.6252       | 1.6787        | 1                      | 16           |
| 415   | 56.0777       | 1.6387        | 2                      | 16           |
| 433   | 56.1682       | 1.6362        | 1                      | 16           |
| 008   | 58.4233       | 1.5783        | 2                      | 2            |
| 440   | 58.7754       | 1.5697        | 2                      | 4            |
| 118   | 60.4265       | 1.5307        | 4                      | 8            |
Table 8: Calculated crystal parameters of CH$_3$NH$_3$PbI$_3$.

| Structure type | Crystal system | Space group | Lattice constant (Å) | V (Å$^3$) | Z | V/Z (Å$^3$) | Method          | Temperature (K) | Reference |
|---------------|----------------|-------------|----------------------|-----------|---|------------|----------------|----------------|-----------|
| α             | Pseudo-cubic   | a = 6.29, b = 6.23, c = 6.37 | 252.4 | 1 | 252.4 | DFT/PBEsol | 352             | 164       |
| β             | Tetragonal     | a = 8.70, b = 8.72, c = 12.83 | 973.3 | 4 | 243.4 | DFT/PBEsol | 180             | 164       |
| γ             | Orthorhombic   | a = 9.04, b = 12.66, c = 8.35 | 955.6 | 4 | 238.9 | DFT/PBEsol | 100             | 164       |
| γ             | Orthorhombic   | pnma        | a = 8.850, b = 12.688, c = 8.564 | 961.6 | 4 | 240.4 | VASP          | 10          | 136       |

Figure 12: Structural models of cubic CH$_3$NH$_3$PbI$_3$ observed along (a) [100], (b) [110], (c) [111], and (d) [210].

Computed crystal parameters of the CH$_3$NH$_3$PbI$_3$ with cubic, tetragonal, and orthorhombic structures, which were calculated by first principle DFT calculation, are summarized in Table 8. Although these parameters indicate similar values to the experimental data, listed in Table 3, there seems some structural distortion for the cubic and tetragonal structures after structural optimization, which would be due to the anisotropy of the CH$_3$NH$_3^+$.

5 Electron diffraction of cubic and tetragonal CH$_3$NH$_3$PbI$_3$

As described in section 2, the electron diffraction patterns of perovskite crystals in nanoscale regions can be obtained, and the diffraction reflections should be indexed for the structure analysis. To analyze the crystal structures by electron diffraction, several important crystal directions with low indices should be chosen and calculated. Figure 12 is structural models of cubic CH$_3$NH$_3$PbI$_3$.
Figure 13: Calculated electron diffraction patterns of cubic CH$_3$NH$_3$PbI$_3$ along (a) [100], (b) [110], (c) [111], and (d) [210].

Figure 14: Structural models of tetragonal CH$_3$NH$_3$PbI$_3$ observed along (a) [001], (b) [100], (c) [021], and (d) [221].

Figure 15: Calculated electron diffraction patterns of tetragonal CH$_3$NH$_3$PbI$_3$ along (a) [001], (b) [100], (c) [021], and (d) [221].

directions, which correspond to [100], [110], [111], and [210], respectively, of the cubic CH$_3$NH$_3$PbI$_3$ in Figure 12. For the tetragonal phase, deviations of the iodine site are decreased, and the mean positions of CH$_3$NH$_3$ are shown in the projected model. The resultant electron diffraction patterns of the tetragonal CH$_3$NH$_3$PbI$_3$ computed along the 4 different crystal directions are shown in Figure 15. As indicated by arrows in Figure 15(c), the symmetry of diffraction reflections for the tetragonal perovskite is not perfect 6-fold symmetry, and is lowered than that of the cubic perovskite. Several reflections in Figure 15 have dissimilar reflection intensities compared with those in Figure 13, which is due to the reduction of the crystal symmetries of the CH$_3$NH$_3$PbI$_3$ crystal.

Diffraction reflections of the perovskite crystals are observed in the experimental diffraction pattern in Figure 3(b), which is indicated by cubic indices with P. Both computed electron diffraction patterns of the cubic CH$_3$NH$_3$PbI$_3$ projected along the [210] (Figure 13(d)) and the tetragonal CH$_3$NH$_3$PbI$_3$ projected along the [221] direction (Figure 15(d)) agree well with the observed diffraction pattern in Figure 3(b), as indicated by the rectangles with blue lines. Intensity ratios of the reflections in the experimental diffraction pattern may resemble those of the tetragonal phase in Figure 15(d).

TEM is a very useful tool for structural analysis of nanostructured materials such as perovskite compounds. Since the CH$_3$NH$_3$PbI$_3$ and related halide compounds are unstable under the vacuum or at raised temperatures,
specimen damage by electron beam bombardment must be avoided. Several TEM analysis studies on the perovskite halide compounds for solar cells have been reported, and the crystal structures and nanostructures were investigated by the structural images and electron diffraction patterns [118, 165, 166].

6 Crystal structures of HC(NH₂)₂PbI₃

In addition to the most standard CH₃NH₃PbI₃ perovskite compound, HC(NH₂)₂PbI₃ and mixed MAPbI₃/FAPbI₃ perovskite compounds are also widely used and studied. The structural models of the HC(NH₂)₂PbI₃ crystals are summarized and shown in Figure 16. High photoconversion efficiencies were reported for α-HC(NH₂)₂PbI₃ with a cubic structure [167, 168], which is a stable black phase at room temperature, as shown in Figure 16(a). When the α-HC(NH₂)₂PbI₃ crystal is cooled below ~200 K, the α-phase is transformed to β-HC(NH₂)₂PbI₃ with a trigonal structure, as shown in Figure 16(b) and 16(c). On the other hand, the α-HC(NH₂)₂PbI₃ phase is converted to the δ-HC(NH₂)₂PbI₃ phase with a hexagonal structure in the presence of a liquid interface (e.g., during spin-coating) below 360 K [167], as shown in Figure 16(d). This cubic-to-hexagonal structural phase transition could be attributed to the Gibbs free energy because of the isotropic rotations of the HC(NH₂)₂⁺ cations.

Local arrangements of the trigonal planar HC(NH₂)₂⁺ cations in the unit cell were determined by neutron diffraction [167], as shown in Figure 17. The HC(NH₂)₂⁺ cation exists at the central mirror plane of the cube, and the HC(NH₂)₂⁺ is aligned along twelve different directions (Figure 17(a)). Then, the C–H bonding is aligned to face-center of the unit cell, as observed in Figure 17(b). On the other hand, hydrogen atoms of the NH₂ group interact with the iodide ions of PbI₂ [167]. ADP ellipsoids shown at 50% probability of the model in Figure 16(a) are shown in Figure 17(c). Although displacements of iodine ions are observed, the displacements are smaller compared with those of MAPbI₃ observed in Figure 6(e).

Calculated XRD patterns of α-, β-, and δ-HC(NH₂)₂PbI₃ crystals with cubic, trigonal, and hexagonal structures [161] are shown in Figure 18, and computed XRD parameters of the cubic and hexagonal FAPbI₃ are summarized and listed in Tables 9 and 10, respectively. In the cubic α-FAPbI₃ phase, site occupancies of C–H and N–H are 1/6 and 1/12, respectively. For the δ-FAPbI₃, the occupancies were set at 2/3 for N and 1 for C. The 100 reflection position at lower 20 angles is characteristic of the δ-FAPbI₃ phase [161], and can be applied for distinction between the α- and δ-phases. Several small reflections appear in the diffraction pattern for the β-FAPbI₃, which

![Figure 16: Structural models of (a) α-HC(NH₂)₂PbI₃ along [100], β-HC(NH₂)₂PbI₃ along (b) [001] and (c) [1T2], and (d) δ-HC(NH₂)₂PbI₃ along [001].](image-url)

| Index | 2θ(°)   | d-spacing (Å) | Relative intensity (%) | Multiplicity |
|-------|---------|---------------|------------------------|--------------|
| 1 0 0 | 13.9083 | 6.3620        | 100                    | 6            |
| 1 1 0 | 19.7183 | 4.4986        | 7                      | 12           |
| 1 1 1 | 24.2105 | 3.6731        | 13                     | 8            |
| 2 0 0 | 28.0270 | 3.1810        | 68                     | 6            |
| 2 1 0 | 31.4157 | 2.8452        | 62                     | 24           |
| 2 1 1 | 34.5037 | 2.5973        | 3                      | 24           |
| 2 2 0 | 40.0527 | 2.2493        | 51                     | 12           |
| 2 2 1 | 42.5969 | 2.1207        | 28                     | 24           |
| 3 0 0 | 42.5969 | 2.1207        | 7                      | 6            |
| 3 1 0 | 45.0236 | 2.0118        | 2                      | 24           |
| 3 1 1 | 47.3516 | 1.9182        | 5                      | 24           |
| 2 2 2 | 49.5956 | 1.8366        | 18                     | 8            |
| 3 2 0 | 51.7671 | 1.7645        | 16                     | 24           |
| 3 2 1 | 53.8755 | 1.7003        | 2                      | 48           |
| 4 0 0 | 57.9334 | 1.5905        | 9                      | 6            |
| 3 2 2 | 59.8950 | 1.5430        | 11                     | 24           |
| 4 1 0 | 59.8950 | 1.5430        | 10                     | 24           |
Figure 17: (a) Averaged and (b) local structural models of HC(NH$_2$)$_2$PbI$_3$. (c) Atomic displacement parameter ellipsoids shown at 50% probability of (a).

Table 10: Calculated X-ray diffraction parameters of hexagonal δ-HC(NH$_2$)$_2$PbI$_3$. Equivalent indices were combined. For space group $P6_3/mc$ (186), $a = 8.6603(14)$ Å, $c = 7.9022(6)$ Å at 293 K.

| Index  | 2θ (°) | d-spacing (Å) | Relative intensity (%) | Multiplicity |
|--------|--------|---------------|------------------------|--------------|
| 1 0 0  | 11.7898| 7.5000        | 100                    | 6            |
| 1 0 1  | 16.2806| 5.4399        | 13                     | 12           |
| 1 1 0  | 20.4935| 4.3301        | 5                      | 6            |
| 0 0 2  | 22.4840| 3.9511        | 5                      | 2            |
| 1 0 2  | 25.4594| 3.4917        | 13                     | 12           |
| 2 0 1  | 26.2837| 3.3879        | 56                     | 12           |
| 1 1 2  | 30.6049| 2.2493        | 31                     | 12           |
| 2 1 0  | 31.5343| 2.8347        | 20                     | 12           |
| 2 0 2  | 32.9019| 2.7200        | 37                     | 12           |
| 2 1 1  | 33.5583| 2.6683        | 4                      | 24           |
| 3 0 0  | 35.8908| 2.5000        | 1                      | 6            |
| 1 0 3  | 36.1114| 2.4852        | 2                      | 12           |
| 2 1 2  | 39.0757| 2.3033        | 6                      | 24           |
| 2 2 0  | 41.6820| 2.1651        | 17                     | 6            |
| 2 0 3  | 41.8766| 2.1555        | 9                      | 12           |
| 3 0 2  | 42.7669| 2.1126        | 10                     | 12           |
| 3 1 0  | 43.4686| 2.0801        | 7                      | 12           |

Figure 18: Calculated X-ray diffraction patterns of $\alpha$-, $\beta$-, and $\delta$-HC(NH$_2$)$_2$PbI$_3$. 
7 Elemental substituted perovskites and double perovskites

In previous sections, two most standard crystal structures of CH$_3$NH$_3$PbI$_3$ and HC(NH$_2$)$_2$PbI$_3$ were described. In addition to these standard MAPbI$_3$ and FAPbI$_3$ halide perovskites, elemental substitution is possible for ABX$_3$ type perovskite crystals as described in section 3, which provide various compositions, structures and electronic properties. Numerous kinds of elemental substituted perovskite halides have been reported, which are summarized and listed in Table 11. Partial elemental substitutions are often introduced for these MAPbI$_3$ and FAPbI$_3$ perovskite crystals to control the optoelectronic properties. For example, iodine atoms (X site) can be replaced by Br and Cl atoms; MA or FA (A site) can be substituted with Cs and Rb; and Pb (B site) can be substituted with Sn, Ge, Sb, Cu and other elements.

Examples of elemental substitutions are shown in the calculated XRD patterns of CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbCl$_3$ in Figure 19, indicating the effect of halogen substitution. When the Br$^-$ ions are substituted by Cl$^-$ ions, the diffraction peaks of CH$_3$NH$_3$PbCl$_3$ are shifted to higher angles compared with those of CH$_3$NH$_3$PbBr$_3$. Furthermore, when Pb$^{2+}$ ions are substituted by Sn$^{2+}$ ions, the diffraction intensities of CH$_3$NH$_3$SnCl$_3$ fairly change compared with those of CH$_3$NH$_3$PbCl$_3$. CH$_3$NH$_3^+$ ions can also be substituted by Cs$^+$ ions, as shown in the structural models of CsSnI$_3$ and CsPbBr$_3$ in Figure 20(a) and 20(b), respectively.

Calculated XRD patterns of HC(NH$_2$)$_2$SnI$_3$, CH$_3$NH$_2$SnI$_3$, and CsSnI$_3$ are shown in Figure 21, which indicate the A site substitutions in the ABX$_3$ perovskite. The diffraction pattern of MASnI$_3$ is similar to that of FASnI$_3$, whereas the diffraction peak intensities of CsSnI$_3$ are fairly different from those of the MASnI$_3$ and FASnI$_3$, despite almost the same diffraction angles. Although large crystals of the Cs-based perovskites have not been synthesized and grown easily, nanoparticles can be produced, and quantum dots of the Cs-based perovskite halides have been investigated [180, 181].

Figure 19: Calculated X-ray diffraction patterns of CH$_3$NH$_3$PbBr$_3$, CH$_3$NH$_3$PbCl$_3$ and CH$_3$NH$_3$SnCl$_3$ with cubic structures.

Figure 20: Structural models of (a) CsSnI$_3$ and (b) CsPbBr$_3$. 
Table 11: Crystal systems of various perovskite halide compounds.

| Compound | Crystal system | Space group | Lattice parameters (Å) and degrees | Z | Temperature (K) | Reference |
|----------|----------------|-------------|-----------------------------------|---|----------------|-----------|
| CH$_3$NH$_3$PbBr$_3$ | Cubic | Pm̅3m | $a = 5.933(2)$ | 1 | 298 | 134 |
| | Tetragonal | I4/mcm | $a = 8.3381(3)$, $c = 11.8587(5)$ | 4 | 220 | 169 |
| | | P4$_1$/mmm | $a = 5.894(2)$, $c = 5.861(2)$ | 1 | 150-155 | 156 |
| | Orthorhombic | Pn̅a$_2_1$ | $a = 7.979(1)$, $b = 8.580(2)$, $c = 11.849(2)$ | 4 | < 145 | 156 |
| CH$_3$NH$_3$PbCl$_3$ | Cubic | Pm̅3m | $a = 5.666(2)$ | 1 | 200 | 134 |
| | Tetragonal | P4$_1$/mmm | $a = 5.656$, $c = 5.630$ | 2 | 173-179 | 156 |
| | Orthorhombic | P2$_2_1$P2$_2_1$P2$_1$ | $a = 5.673$, $b = 5.628$, $c = 11.182$ | 2 | < 173 | 156 |
| CH$_3$NH$_3$SnI$_3$ | Tetragonal | P4mm | $a = 6.2302(10)$, $c = 6.2316(11)$ | 1 | 293 | 161 |
| CH$_3$NH$_3$SnI$_3$ | Tetragonal | I4cm | $a = 8.7577(15)$, $c = 12.429(3)$ | 4 | 200 | 161 |
| CH$_3$NH$_3$SnBr$_3$ | Tetragonal | P4mm | $a = 5.837(1)$, $c = 5.853(4)$ | 1 | 41 | |
| CD$_3$ND$_3$GeCl$_3$ | Cubic | Pm̅3m | $a = 5.6917(2)$ | 1 | 475 | 170 |
| | Orthorhombic | $R3m$ | $a = 5.6784(1)$, $a = 90.945(1)^\circ$ | 1 | 370 | 170 |
| | Monoclinic | P1c1 | $a = 5.718(1)$, $b = 8.236(1)$, $c = 7.938(1)$, $\beta = 91.90(1)^\circ$ | 2 | 318 | 171 |
| | Triclinic | P1 | $a = 5.726$, $b = 8.227$, $c = 7.910$, $\alpha = 90.40^\circ$, $\beta = 93.08^\circ$, $\gamma = 90.15^\circ$ | 2 | 297 | 171 |
| HC(NH$_3$)$_2$PbI$_3$ | Trigonal | P3 | $a = 17.7914(8)$, $b = 10.9016(6)$ | 12 | 150 | 161 |
| HC(NH$_3$)$_2$PbBr$_3$ | Cubic | Pm̅3m | $a = 5.98618(2)$ | 1 | 275 | 172 |
| | | Tetragonal | P4$_1$/mbm | $a = 8.41525(5)$, $c = 5.94735(8)$ | 2 | 175 | 172 |
| | Orthorhombic | Pnma | $a = 8.37433(9)$, $b = 11.8609(1)$, $c = 8.38073(9)$ | 4 | 100 | 172 |
| | Tetragonal | P4$_1$/mbm | $a = 8.86227(2)$, $c = 6.24892(2)$ | 2 | 175 | 172 |
| | Orthorhombic | Pnma | $a = 8.81749(8)$, $b = 12.41641(7)$, $c = 8.8578(1)$ | 4 | 100 | 172 |
| | Orthorhombic | Amm2 | $a = 6.3286(10)$, $b = 8.9554(11)$, $c = 8.9463(11)$ | 2 | 340 | 161 |
| | | | | | | |

Lattice constants of several perovskite halide compounds with the ABX$_3$ structure are plotted in Figure 22. Changes in the lattice constants are strongly dependent on the halogen X site substitutions compared with the A or B site substitutions for the ABX$_3$ structure.

In addition to the ordinary elemental substitution, atomic orderings of the substituted elements have also been achieved and reported, which is called double perovskite or elpasolite. The general formula is A$_2$BB’X$_6$, and the ionic valence of B/B’ is 1$^+$/3$^+$ or 2$^+$/2$^+$. One of the examples of the double perovskite structure is Cs$_2$AgBiBr$_6$, and the structural models observed along the [100], [110], and [111] crystal directions are shown in Figure 23(a), (b), and (c), respectively. AgBr$_6$ and BiBr$_6$ octahedra are alternately ordered in the perovskite crystal, as shown in Figure 23(b) and 23(d).

Various double perovskite halide compounds such as Cs$_2$AgInCl$_6$, Cs$_2$NaBiCl$_6$, Cs$_2$KEuCl$_6$, Cs$_2$LiScCl$_4$, (CH$_3$NH$_3$)$_2$AgBiBr$_6$, (CH$_3$NH$_3$)$_2$KBiCl$_6$, Rb$_2$NaCrCl$_6$, and others have been reported, as listed in Table 12, which are all Pb-free compounds. Calculated X-ray diffraction patterns of Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$AgBiBr$_6$ are
Table 12: Crystal systems of various double perovskite halide compounds.

| Compound                        | Crystal system | Space group | Lattice parameters (Å) | Z  | Temperature (K) | Reference |
|---------------------------------|----------------|-------------|------------------------|----|-----------------|-----------|
| Cs₂AgBiBr₆                      | Cubic          | Fm̅3m       | a = 11.2499            | 4  | 300             | 182       |
| Cs₂AgBiCl₆                     | Cubic          | Fm̅3m       | a = 10.7774(2)         | 4  | -               | 183       |
| Cs₂AgInCl₆                     | Cubic          | Fm̅3m       | a = 10.48059(5)        | 4  | 300             | 184       |
| Cs₂NaBiCl₆                     | Cubic          | Fm̅3m       | a = 10.8429(1)         | 4  | RT              | 185       |
| (CH₃NH₃)₂AgBiBr₆               | Cubic          | Fm̅3m       | a = 11.6370(1)         | 4  | 300             | 186       |
| (CH₃NH₃)₂KBICl₆                | Rhombohedral   | R̅̅̅3m      | a = 7.8372(2), c = 20.9938(2) | 3  | 300             | 187       |
| Cs₂NaHoCl₆                     | Cubic          | Fm̅3m       | a = 10.722             | 4  | 294             | 188       |
| Cs₂NaYCl₆                      | Cubic          | Fm̅3m       | a = 10.7275(2)         | 4  | 294             | 188       |
| Cs₂NaCeCl₆                     | Cubic          | Fm̅3m       | a = 10.943(2)          | 4  | -               | 189       |
| Cs₂NaErCl₆                     | Cubic          | Fm̅3m       | a = 10.7089            | 4  | -               | 190       |
| Cs₂NaSmCl₆                     | Cubic          | Fm̅3m       | a = 10.8342            | 4  | -               | 190       |
| Cs₂NaYBr₆                      | Cubic          | Fm̅3m       | a = 11.3047(6)         | 4  | -               | 191       |
| Cs₂LiInCl₆                     | Rhombohedral   | R̅̅̅3m      | a = 7.3184 (4), c = 36.240 (3) | 6  | -               | 191       |
| Cs₂LiLuCl₆                     | Cubic          | Fm̅3m       | a = 10.409             | 4  | -               | 192       |
| Cs₂LiScCl₆                     | Rhombohedral   | R̅̅̅3m      | a = 7.2965 (6), c = 35.989 (4) | 6  | -               | 191       |
| Cs₂LiYCl₆                      | Cubic          | Fm̅3m       | a = 10.4857 (5)        | 4  | -               | 191       |
| Cs₂KBiCl₆                      | Cubic          | Fm̅3m       | a = 11.086 (5)         | 4  | 293             | 193       |
| Cs₂KCrCl₆                      | Cubic          | Fm̅3m       | a = 10.633 (2)         | 4  | -               | 194       |
| Cs₂KEuCl₆                      | Cubic          | Fm̅3m       | a = 11.1633 (3)        | 4  | 296             | 195       |
| Cs₂KLaCl₆                      | Cubic          | Fm̅3m       | a = 11.379 (5)         | 4  | -               | 196       |
| Cs₂KScCl₆                      | Cubic          | Fm̅3m       | a = 10.873 (3)         | 4  | -               | 192       |
| Cs₂KYCl₆                       | Cubic          | Fm̅3m       | a = 11.128 (5)         | 4  | -               | 196       |
| Rb₂Li₃DBr₆                     | Tetragonal     | I4/mmm     | a = 7.699 (5), c = 11.032 (6) | 2  | 293             | 197       |
| Rb₂NaCrCl₆                     | Cubic          | Fm̅3m       | a = 10.131 (2)         | 4  | -               | 194       |
| Rb₂NaTmCl₆                     | Tetragonal     | P4/nmm     | a = 10.530 (4), c = 10.599 (4) | 4  | 295             | 198       |

Figure 21: Calculated X-ray diffraction patterns of HC(NH₃)₂SnI₃, CH₃NH₃SnI₃, and CsSnI₃.

Figure 22: Lattice constants of various ABX₃ perovskite compounds. A = Cs, MA, or FA. B = Ge, Sn, or Pb. X = Cl, Br, or I.

shown in Figure 24. When the Bi³⁺ ions are substituted by In³⁺ ions, the diffraction peaks of Cs₂AgInCl₆ are shifted to higher angles compared with those of Cs₂AgBiCl₆. In addition, when Cl⁻ ions are substituted by Br⁻ ions, the diffraction intensities of Cs₂AgBiBr₆ fairly change compared with those of Cs₂AgBiCl₆.
Figure 23: Structural models of Cs$_2$AgBiBr$_6$ with double perovskite structures, observed along (a) [100], (b) [110], and (c) [111]. (d) Perspective view of the structure.

Figure 24: Calculated X-ray diffraction patterns of Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$AgBiBr$_6$ double perovskites.

MA$^+$ ions can be substituted at the Cs site, and structural models of MA$_2$KBiCl$_6$ double perovskite structures observed along [001] and [100] are shown in Figure 25(a) and 25(b), respectively, in which hydrogen atoms are omitted. Calculated X-ray diffraction patterns of Cs$_2$NaBiCl$_6$, (CH$_3$NH$_3$)$_2$KBiCl$_6$, and (CH$_3$NH$_3$)$_2$AgBiBr$_6$ are shown in Figure 26. If the Cs$^+$ ions are substituted by the MA$^+$ ions, the diffraction peaks of MA$_2$AgBiBr$_6$ are shifted to lower angles compared with those of Cs$_2$NaBiCl$_6$, and the diffraction intensities fairly change. Since the MA$_2$KBiCl$_6$ has a rhombohedral symmetry, the diffraction patterns are completely different from other double perovskite halides with cubic symmetry.

Some of these double perovskite elpasolite compounds are expected to apply to Pb-free solar cells [199–201], and the energy gaps have been reported [187, 199]. Application of the double perovskite elpasolites are also be expected for thermal neutron scintillator materials [202–204]. Other types of double perovskite compounds such
as vacancy-ordered double perovskites and 2-dimensional double perovskites have also been reported, which will be described as low-dimensional perovskites in the next section.

8 Low-dimensional perovskites

Normal perovskite halide compounds, as described in the previous sections, consist of octahedra sharing all vertices with the neighboring octahedra 3-dimensionally. In addition to the common 3-dimensional (3D) perovskites, various perovskite compounds with lower dimensional structures have been reported [199, 205–207], as summarized and listed in Table 13. Like 2-dimensional (2D) superconducting copper oxide perovskites [116, 117], the derivative structures with lower dimensionality could provide finer tunability of the electronic properties [232–236].

For the 0-dimensional (0D) perovskite, all BX$_6$ octahedra are isolated in the perovskite crystal, as shown in Figures 27 and 28. For the Rb$_2$SnCl$_6$ compound in Figure 27, there are insufficient Sn atoms to form RbSn$_{0.5}$Cl$_{1.5}$, and the SnCl$_6$ octahedra are isolated in the crystal with A-site cations occupying the cuboctahedral voids. From the viewpoint of double perovskites, elements with tetravalent cations are incorporated to form 4$^+/0$ double perovskites. This is called vacancy-ordered double perovskites with the general formula of A$_2$BvX$_6$, where the v means vacant positions corresponding to the B’ site for the A$_2$BB’X$_6$ double perovskites. Despite the isolated octahedral BX$_6$ units, the close-packed iodide lattice provides electronic dispersion, and Cs$_2$SnI$_6$ and other perovskites were applied to solar cells [237, 238]. Pb free solar cells such as FA$_4$GeSbCl$_{12}$ have been reported [239], in which the double elements were selected to replace Pb. Cs$_2$Ti$_2$Br$_6$–x vacancy-ordered double perovskite compounds were also reported to have stability and bandgaps between 1.0 and 1.8 eV [240].

On the other hand, excess Cs and insufficient Pb in the Cs$_4$PbBr$_6$ crystal yield the 0D structure, as shown in Figure 28. Another type of 0D perovskite halide structure is shown in Figure 29. Because of the ionic valence of antimony ion (Sb$^{3+}$), the suitable composition of the com-

![Figure 27: Structural models of Rb$_2$SnCl$_6$ with 0-dimensional perovskite structures, observed along (a) [100], (b) [110], and (c) [111]. (d) Perspective view of the structure.](image)

![Figure 28: Structural models of Cs$_4$PbBr$_6$ with 0-dimensional perovskite structures, observed along (a) [001], (b) [100], and (c) [210]. (d) Perspective view of the structure.](image)

![Figure 29: Structural models of Cs$_3$Sb$_2$I$_9$ with 0-dimensional bioctahedra structures, observed along (a) [001] and (b) [100].](image)
Table 13: Crystal systems of low-dimensional perovskite crystals.

| Compound            | Dimensionality | Crystal system | Space group | Lattice parameters (Å) and degrees | Z  | Reference |
|---------------------|----------------|----------------|-------------|-----------------------------------|----|-----------|
| C_{6}N_{2}H_{16}PbI_{4} | 2              | Monoclinic     | P6            | a = 10.6999(13), b = 12.5429(9), c = 12.5289(13), β = 89.984(9)° | 4  | 208       |
| (C_{6}N_{2}H_{16})(CH_{3}NH_{3})PbI_{2}   | 2              | Monoclinic     | Cc           | a = 23.1333(7), b = 8.8365(3), c = 8.8354(3), β = 90°  | 4  | 208       |
| (C_{6}N_{2}H_{16})(CH_{3}NH_{3})PbI_{4}   | 2              | Monoclinic     | Cc           | a = 8.8587(18), b = 8.8571(18), c = 58.915(12), β = 90° | 4  | 208       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{2}(CH_{3}NH_{3})PbF_{2}   | 2              | Orthorhombic   | Cmcm         | a = 8.9470(4), b = 39.347(2), c = 8.8589(6)       | 4  | 209       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{2}(CH_{3}NH_{3})PbI_{2}   | 2              | Orthorhombic   | Ama2         | a = 8.9275(6), b = 51.959(4), c = 8.8777(6), β = 88.16(4) | 4  | 209       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{2}(CH_{3}NH_{3})PbI_{4}   | 2              | Orthorhombic   | Ama2         | a = 8.9274(6), b = 64.36(4), c = 8.8816(4)       | 4  | 209       |
| (CH_{3}NH_{3})_{2}CuCl_{6}   | 2              | Monoclinic     | P2/c         | a = 7.2574(8), b = 7.3504(1), c = 9.9688(5), β = 111.20° | 1  | 210       |
| (CH_{3}NH_{3})_{2}CuCl_{2}Br_{2}   | 2              | Orthorhombic   | Cmca         | a = 7.3194(4), b = 7.3281(4), c = 19.1344(1)   | 2  | 210       |
| (C_{6}H_{5}(CH_{2})_{3}NH_{3})_{3}CdCl_{4} | 2              | Orthorhombic   | Aba2         | a = 7.4444(2), b = 38.8965(3), c = 7.3737(2) | 4  | 211       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{2}AglnCl_{6} | 2 + double perovskite | Triclinic | PT          | a = 7.454(3), b = 7.866(3), c = 24.629(8), α = 90.141(10)°, β = 89.992(10)°, γ = 90.049(11)° | 2  | 212       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{2}AglnBr_{6} | 2 + double perovskite | Monoclinic | C2/m         | a = 24.5633(13), b = 7.7838(4), c = 8.2501(4), β = 90.091(2)° | 2  | 212       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{2}AgBiBr_{6} | 2 + double perovskite | Monoclinic | C2/m         | a = 24.503(7), b = 7.964(2), c = 8.3842(2), β = 90.045(9)° | 2  | 212       |
| (NH_{3})(CH_{3}NH_{3})_{2}AgBiBr_{6} | 2 + double perovskite | Triclinic | PT          | a = 8.1018(3), b = 8.2433(3), c = 9.6813(4), α = 101.1960(10)°, β = 92.055(2)°, γ = 90.3960(10)° | 1  | 212       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{3}AgBiBr_{6} | 2 + double perovskite | Monoclinic | P2/m         | a = 8.2024(7), b = 8.1797(6), c = 21.1217(18), β = 101.195(3)° | 1  | 212       |
| (CH_{3}(CH_{2})_{3}NH_{3})_{3}CsAgBiBr_{7} | 2 + double perovskite | Monoclinic | P21/m        | a = 8.053(6), b = 7.997(3), c = 18.536(8), β = 102.503(11)° | 2  | 212       |
| α-Cs_{5}Sb_{2}Cl_{6} | 2              | Trigonal       | P321         | a = 7.633, c = 9.345 | 1  | 213       |
| β-Cs_{5}Sb_{2}Cl_{6} | 1              | Orthorhombic   | Pna          | a = 7.630(20), b = 13.079(3), c = 18.663(4)       | 1  | 214       |
| CsTiI_{3} | 1              | Hexagonal      | P6_{3}/mmmc  | a = 8.214(2), b = 6.789(2)       | 2  | 215       |
| CsTiBr_{3} | 1              | Hexagonal      | P6_{3}/mmmc  | a = 7.656(1), b = 6.357(1)       | 2  | 216       |
| CsTiCl_{3} | 1              | Hexagonal      | P6_{3}/mmmc  | a = 7.3086(7), b = 6.0670(8)       | 2  | 217       |
| Cs_{24}H_{35}S_{2}N_{4}PbI_{5} | 1              | Monoclinic     | P2_{1}/c      | a = 17.553(2), b = 8.710(1), c = 27.122(5), β = 97.57(2)° | 4  | 218       |
| Cs_{2}SnI_{6} | 0              | Cubic          | Fm3m         | a = 11.6276(9)       | 4  | 161       |
| Cs_{2}SnBr_{6} | 0              | Cubic          | Fm3m         | a = 10.7435(2)       | 4  | 219       |
| Cs_{3}SnCl_{6} | 0              | Cubic          | Fm3m         | a = 10.3552(2)       | 4  | 220       |
| Cs_{3}SnBr_{6} | 0              | Cubic          | Fm3m         | a = 13.7219(2), b = 17.3153(3)       | 6  | 221       |
| Cs_{3}PbCl_{6} | 0              | Cubic          | Fm3m         | a = 13.182(5), b = 16.641(5)       | 6  | 222       |
| Cs_{3}PbI_{6} | 0              | Cubic          | Fm3m         | a = 11.473(3)       | 4  | 223       |
| Cs_{3}TiCl_{6} | 0              | Cubic          | Fm3m         | a = 10.23       | 4  | 224       |
| Cs_{3}TeI_{6} | 0              | Cubic          | Fm3m         | a = 11.7088(1)       | 4  | 225       |
| Rb_{2}SnI_{6} | 0              | Cubic          | Fm3m         | a = 8.07056(6), b = 11.76501(1)       | 4  | 226       |
| Rb_{2}SnCl_{6} | 0              | Cubic          | Fm3m         | a = 10.137(2)       | 4  | 227       |
| (NH_{3})_{2}PtI_{6} | 0              | Cubic          | Fm3m         | a = 11.158(8)       | 4  | 228       |
| K_{3}PdCl_{6} | 0              | Cubic          | Fm3m         | a = 9.743(3)       | 4  | 229       |
| Cs_{2}Sb_{2}I_{9} | 0-dimer        | Hexagonal      | P6_{3}/mmmc  | a = 8.349(1), b = 20.916(1)       | 2  | 230       |
| Cs_{3}Bi_{2}I_{9} | 0-dimer        | Monoclinic     | C2/c         | a = 8.346(6), b = 14.472(9), c = 21.10(1), β = 91.00(6)° | 4  | 231       |
compound is Cs$_3$Sb$_2$I$_9$, which satisfies the charge neutral condition. The faces of two Sbl$_6$ octahedra are connected to each other, and the Sbl$_6$ dimers or biocahedra are isolated in the crystal.

Calculated XRD patterns of Cs$_4$PbBr$_6$, Rb$_2$SnCl$_6$, and Cs$_3$Sb$_2$I$_9$, with trigonal, cubic, and hexagonal symmetries, respectively, are shown in Figure 30. For the Rb$_2$SnCl$_6$ compound, Miller indices of the diffraction patterns are similar to those of ordinary double perovskite structures (Figure 24) since the crystal system belongs to the same space group of $Fmar{3}m$. However, the reflection intensities are different from those of common double perovskite, which is due to the vacant B’ site for the A$_2$BB’X$_6$ double perovskite structure. Diffraction patterns of Cs$_4$PbBr$_6$ and Cs$_3$Sb$_2$I$_9$ are fairly different from that of Rb$_2$SnCl$_6$, and a 002 reflection appears at a 2θ of 8.4° (not shown in Figure 30) for the Cs$_3$Sb$_2$I$_9$ crystal.

In addition to the perovskite compounds having a dimer octahedron, 1-dimensional continuously connected octahedra exist in CsTiCl$_3$, as shown in Figure 31. Out of the eight faces of one TiCl$_6$ octahedron, two opposite faces are directly connected to the two neighboring octahedra along the [001] direction, and the connected chain is infinitely continuous.
Figure 32 is a structural model of orthorhombic β-Cs$_3$Sb$_2$Cl$_9$ with a 1-dimensional (1D) perovskite structure, observed along three main directions. Two octahedra are arranged sharing their vertex atoms, as observed in Figure 32(b), and these octahedral pairs or dimers are 1-dimensionally arranged along the observation direction of [010]. Two-dimensional perovskite halide structures such as trigonal α-Cs$_3$Sb$_2$Cl$_9$ are also reported, as shown in Figure 33(a). Vertex Cl atoms of SbCl$_6$ octahedra are continuously connected in a 2D manner. 2D copper perovskites MA$_2$CuCl$_x$Br$_{4-x}$ were also synthesized as Pb-free light harvesters [241, 242], as shown in Figure 33(b).

XRD patterns of the 2D α-Cs$_3$Sb$_2$Cl$_9$, 1D β-Cs$_3$Sb$_2$Cl$_9$, and 1D CsTiCl$_3$ perovskite compounds were calculated, as shown in Figure 34. Various reflections are observed, which reflects their unit cells. Although the CsTiCl$_3$ is called vacancy-ordered double perovskites, the XRD pattern is dissimilar to those of double perovskites in Figure 24, which is due to the lack of B’ site atoms.

Other types of 2D layered perovskites were also reported, which is called the Dion-Jacobson (DJ) structure [208]. The lead iodides with DJ perovskite structures have the standard formula of A(MA)$_{n-1}$Pb$_n$I$_{3n+1}$. C$_6$N$_2$H$_{16}$PbI$_4$, (C$_6$N$_2$H$_{16}$)(CH$_3$NH$_3$)$_2$Pb$_2$I$_7$, and (C$_6$N$_2$H$_{16}$)(CH$_3$NH$_3$)$_3$Pb$_3$I$_{13}$ with the 2D DJ perovskite structures are shown in Figure 35. The organic molecules isolate the PbI$_6$ octahedra, and the 2D layered structure is formed. XRD patterns for C$_6$N$_2$H$_{16}$PbI$_4$, (C$_6$N$_2$H$_{16}$)(CH$_3$NH$_3$)$_2$Pb$_2$I$_7$, and (C$_6$N$_2$H$_{16}$)(CH$_3$NH$_3$)$_3$Pb$_3$I$_{13}$ were calculated as shown in Figure 36, and several diffraction reflections are observed at 2θ angles lower than 10°. This indicates that 2D DJ perovskite compounds have larger lattice constants with long periodicity compared with the standard perovskite halides, as observed in the structural models in Figure 35.
Crystal structures of perovskite halide compounds used for solar cells

Figure 35: Structural models of (a) C$_6$N$_2$H$_{16}$PbI$_4$, (b) (C$_6$N$_2$H$_{16}$)(CH$_3$NH$_3$)$_2$PbI$_7$, and (c) (C$_6$N$_2$H$_{16}$)(CH$_3$NH$_3$)$_3$Pb$_4$I$_{13}$ with 2-dimensional DJ perovskite structures.

Other 2D perovskites with the Ruddlesden-Popper structure were also reported [209]. These perovskite compounds consist of inorganic perovskite layers inserted with butylammonium cations, and they have the general formula (CH$_3$(CH$_2$)$_3$NH$_3$)$_2$PbnI$_{3n+1}$ ($n$ = 1, 2, 3, 4, $\infty$). The perovskite iodides of (CH$_3$(CH$_2$)$_3$NH$_3$)$_2$(CH$_3$NH$_3$)$_2$Pb$_2$I$_7$ ($n$ = 2), (CH$_3$(CH$_2$)$_3$NH$_3$)$_2$(CH$_3$NH$_3$)$_3$Pb$_2$I$_{10}$ ($n$ = 3), and (CH$_3$(CH$_2$)$_2$NH$_2$(CH$_3$NH$_3$)$_3$Pb$_2$I$_{13}$ ($n$ = 4) are shown in Figure 37(a), (b), and 37(c), respectively. Comparing the structural models of the 2D DJ perovskite structures in Figure 35, PbI$_6$ octahedra in the Ruddlesden-Popper 2D structure are observed to have an anti-phase arrangement at the sides of the inserted spacer.

In addition to the above 2D perovskites, 2D double perovskite halides were synthesized by incorporating organic spacer cations such as propylammonium (PA), octylammonium (OCA), and 1,4-butylammonium (BDA) into standard 3D double perovskites [212]. Figure 38(a,b), (c), (d), and 38(e) show structural models of (NH$_3$(CH$_2$)$_4$NH$_3$)$_2$AgBiBr$_8$ (BDA$_2$AgBiBr$_8$), (CH$_3$(CH$_2$)$_7$NH$_3$)$_4$AgBiBr$_8$ (OCA$_4$AgBiBr$_8$), (CH$_3$(CH$_2$)$_2$NH$_3$)$_4$AgInCl$_8$ (PA$_4$AgInCl$_8$), and (CH$_3$(CH$_2$)$_2$NH$_3$)$_2$CsAgBiBr$_7$ (PA$_2$CsAgBiBr$_7$) with 2-dimensional double perovskite structures, respectively. The general formulas of the single-layered Ruddlesden-Popper type and single-layered Dion–Jacobson type are A$_4$BB’X$_8$ ($A$ = PA or OCA) and A$_2$BB’X$_8$, respectively. The band gap energy can be tuned by selecting the spacer layer thickness, and the band gaps of PA$_4$AgBiBr$_8$ and PA$_4$AgInCl$_8$ were reported to be ~2.4 and 4.0 eV [212]. Most of the reported bandgap values would be related with the structural dimensionality [199], and the perovskite crystals with lower dimensionality tend to have wider bandgaps.

9 Actual microstructures of highly (100)-oriented thin films and dendrites

In the previous sections, crystal structures of various perovskite halide compounds were described, which directly
Figure 37: Structural models of (a) \((\text{CH}_3\text{(CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{PbI}_7\), (b) \((\text{CH}_3\text{(CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{I}_{10}\), and (c) \((\text{CH}_3\text{(CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}\) with 2-dimensional Ruddlesden-Popper perovskite structures.

Figure 38: Structural models of (a, b) \((\text{NH}_3\text{(CH}_2)_4\text{NH}_3)_2\text{AgBiBr}_8\), (c) \((\text{CH}_3\text{(CH}_2)_7\text{NH}_3)_4\text{AgBiBr}_8\), (d) \((\text{CH}_3\text{(CH}_2)_2\text{NH}_3)_4\text{AgInCl}_8\), and (e) \((\text{CH}_3\text{(CH}_2)_2\text{NH}_3)_2\text{CsAgBiBr}_7\) with 2-dimensional double perovskite structures.
would be improved by doping Cl [15, 85]. The Cl-added perovskite CH₃NH₃PbI₃(Cl) was spin-coated on the mesoporous TiO₂ layer. An air-blow method was introduced during the spin-coating, and then, the devices were heated at 140 °C to form perovskite halides [246]. When decaphenylcyclopentaasilane is used over the perovskite layer, the annealing temperature can be raised to ~200°C, and the devices show excellent stability [97].

Optical microscope (OM) images of the CH₃NH₃PbI₃(Cl) cells are shown in Figure 40 [246]. As shown in Figure 40(a), particle sizes are in the range of 5–10 μm for the perovskite grains without NH₄Cl. The particle sizes of the perovskite grains were decreased by addition of NH₄Cl to the perovskite, and network-like microstructures are observed, as shown in Figure 40(b), which would possibly increase the conversion efficiency. A scanning electron microscope (SEM) image is also shown in Figure 40(a), and the inclined crystal surface is observed. Elemental mapping images by energy dispersive spectroscopy indicate that the particles observed in Figure 40 correspond to the CH₃NH₃PbI₃ perovskite compound. Atomic compositions were estimated by the energy dispersive spectroscopy analysis [246], which indicates that the Cl would be doped into the CH₃NH₃PbI₃ compounds, as listed in Table 14.

As seen in Figure 41, diffraction intensities of 100 and 200 reflections were enormously enhanced to more than 100 times by introducing NH₄Cl and air blow. The diffraction intensity ratio I₁₀₀/I₂₁₀ was measured and summarized, as listed in Table 14. If the CH₃NH₃PbI₃ perovskite grains are randomly oriented, the I₁₀₀/I₂₁₀ value should be 2.1, as shown in Table 14. The orientation index I₁₀₀/I₂₁₀ is 61 for the cell fabricated using air blow and without NH₄Cl, which indicates that the perovskite grains are preferentially (100)-aligned against the cell substrate. The orientation index I₁₀₀/I₂₁₀ was further enhanced to 3600 by the addition of NH₄Cl, which is 1700 times higher than that of randomly aligned perovskite grains. The cell fabricated with NH₄Cl and without PbCl₂ or air blow provided an orientation index I₁₀₀/I₂₁₀ of 2.8, which indicates the most of the perovskite grains are randomly aligned in the thin film configuration. The orientation indices of

Figure 39: Calculated X-ray diffraction patterns of (NH₄(CH₃)₂NH₃)₂AgIBr₃, (NH₄(CH₃)₂NH₃)₂AgInCl₃, and (NH₄(CH₃)₂NH₃)₂CsAgIBr₃ with 2-dimensional double perovskite structures.

influence the semiconductor and photovoltaic properties. On the other hand, the morphology of perovskite thin films also strongly affects the photovoltaic properties [83, 84, 243]. Wide interfacial areas between n-type TiO₂ electron transport layers and the perovskite layers can promote charge separation, which contributes to the increase of the short circuit current density. Homogeneous and smooth surface/interface structures of the perovskite layers would improve the fill factors and open circuit voltages [99]. Crystal growth and crystallization of the perovskite compounds during annealing are also important and have been investigated [244–246].

Effects of adding ammonium chloride (NH₄Cl) to perovskite CH₃NH₃PbI₃(Cl) solar cells fabricated by an air blowing method are described here [246]. NH₄Cl has a role of surfactant, which would facilitate forming homogeneous perovskite surface structures [83, 243, 247]. In addition, the carrier diffusion length in the perovskite halides would be improved by doping Cl [15, 85]. The Cl-added perovskite halide compound is designated as CH₃NH₃PbI₃(Cl) here.

For the perovskite layer, a mixture solution containing CH₃NH₃I (190.7 mg), PbCl₂ (111.2 mg) and NH₄Cl (0–5 mg) was arranged [248–251], and the solution containing

\[ \text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl}) \]
Table 14: Ratios of 100 diffraction intensities \( (I_{100}) \) to 210 diffraction intensities \( (I_{210}) \) and FTO substrate diffraction intensities \( (I_{FTO}) \), for the perovskite crystals. Compositions of the solar cells as measured by EDS.

| NH\(_4\)Cl (mg) | \( I_{100}/I_{210} \) | \( I_{100}/I_{FTO} \) | Pb (at.%) | I (at.%) | Cl (at.%) | C : N (at.%) |
|----------------|----------------------|----------------------|-----------|---------|-----------|-------------|
| Calculation*   | 2.08                 | -                    |           |         |           |             |
| 0              | 69                   | 51                   | 24.3      | 71.7    | 4.0       | 61.9 : 38.1 |
| 1              | 510                  | 170                  | 24.0      | 71.4    | 4.7       | 61.7 : 38.3 |
| 3              | 3400                 | 280                  | 24.4      | 71.1    | 4.6       | 61.8 : 38.2 |
| 5              | 3600                 | 270                  | 24.1      | 70.2    | 5.7       | 61.8 : 38.2 |
| 5**            | 2.8                  | 0.40                 | 24.0      | 71.2    | 4.8       | 52.0 : 48.0 |

*Calculated from randomly oriented cubic CH\(_3\)NH\(_3\)PbI\(_3\) crystals.

**No air blowing or PbCl\(_2\).

Figure 40: (a) Optical microscope images, SEM images and corresponding elemental mapping images of the CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) cell (a) without NH\(_4\)Cl and containing 5 mg of NH\(_4\)Cl.

\( I_{100}/I_{FTO} \) are also listed in Table 14, and the \( I_{100}/I_{FTO} \) also increased by using the NH\(_4\)Cl and air blow.

Two formation mechanisms were proposed for the highly (100)-aligned perovskite thin films on the mesoporous TiO\(_2\). The first mechanism is air blow-driven crystal growth of the perovskite grains. When the precursor solution crystallizes into the perovskite grains, rapid heating using air blowing promotes oriented-crystallization of the perovskite grains on the mesoporous TiO\(_2\). The (100) of the cubic perovskite structure has low surface energy, which facilitates the crystal growth of (100)-aligned grains. The highly aligned grains reduce the area of high-angle grain boundaries, which induces decrease of the series resistance and increase of the open-circuit voltage. Another formation mechanism is a surfactant effect of NH\(_4\)Cl, which enhanced the construction of homogeneous crystal-aligned microstructures during heating. Network-like microstructures that connect perovskite grains with nanowire-like crystals are also constructed in the perovskite layer, as observed in the optical microscope image of Figure 40(b). Then, the surface covering ratio and carrier transport efficiency were improved, which resulted in the increase of the fill factor and short-circuit current density. Improvement of the photoconversion efficiencies could be understood by these formation models.
Cl substitution at iodine sites also improves the carrier diffusion in the perovskite halide compounds. Excess CH$_3$NH$_3$Cl is vaporized from the initial stoichiometry of 3(CH$_3$NH$_3$I) + PbCl$_2$ \([248–251]\), and a little remained Cl is substituted at the I site of the CH$_3$NH$_3$PbI$_3$ structure. The doped-Cl lengthens the exciton diffusion length [15, 85], which improves the short-circuit current density. As a result, the constructed (100)-aligned perovskite grains improved the photovoltaic properties.

For the formation of the perovskite compounds in thin film configurations, grain growth due to diffusion limitation by solute elements could be the main factor. Figure 42(a) is an optical transmission microscope image of HC(NH$_2$)$_2$PbI$_3$ on the mesoporous TiO$_2$ and F-doped SnO$_2$ substrate, and the perovskite grains with dark contrast are distributed keeping their distances of ~10 µm [252]. Figures 42(b), 42(c) and 42(d) are also optical microscope images of HC(NH$_2$)$_2$PbI$_{2.85}$Br$_{0.15}$, HC(NH$_2$)$_2$PbIBr$_2$, and HC(NH$_2$)$_2$Pb$_{0.95}$Sb$_{0.05}$I$_3$, respectively [48, 253]. They are FAPbI$_3$ doped with Br and Sb at the I and Pb sites, respectively. By adding a small amount of Br and Sb, perovskite crystals with dendritic structures grew densely, and the surface coverage of the perovskite grains on the cell substrate increased. Due to these dendritic structures, short circuit current densities and photo conversion efficiencies increased. Gibbs-Thomson coefficients and liquidus line gradients were estimated, and the dendrites would be formed by satisfying neutral stable conditions on the grain growth rate by increasing the kinds of solute elements. Fractal dimensions of the dendrite structures in Figures 42(b)-42(d) were calculated to be ~2.8 by using a box-counting method. These dendrite structures would contribute increase of the surface coverage and interfacial area at the interpenetrating pn junction, which provided the higher current densities and conversion efficiencies.

The driving force of grain growth is grain boundary energy, which might be caused by the defects at the grain boundary. Since Pb and Sb could be more stable in the perovskite structure, it is believed that the grain boundary energy would be induced by the diffusion of HC(NH$_2$)$_2$, I, and Br on the surface of the perovskite grain, as illustrated in Figure 42(e). The grain boundary energy ($E_b$) with a scalar form has a same dimension as the interfacial tension ($\sigma$) with a vector form, and can be calculated from the following equation:

$$\Delta G_V = \frac{2E_b V_m}{D}$$

where $\Delta G_V$, $E_b$, $D$, and $V_m$ are the Gibbs free energy, grain boundary energy, grain size, and molar volume, respectively. When the CH$_3$NH$_3$PbI$_3$ decomposes into PbI$_2$ and CH$_3$NH$_3$I, the $\Delta G^0$ was calculated to be 10.2 (kJ mol$^{-1}$) [254]. Grain sizes of perovskite crystals observed perpendicular to the substrates are measured to be ~5 µm in Figures 40 and 42, and the grain boundary energies were estimated to be ~170 J m$^{-2}$. On the other hand, crystallite sizes of these thin films measured parallel to the substrates by XRD were ~50 nm, and the grain boundary energies were estimated to be ~1.7 J m$^{-2}$. Practically, only the surface of the perovskite grains might decompose, and the actual $E_b$ would be smaller than that.

A transition temperature of single crystal of MAPbI$_3$ is ~330 K as described in section 4, which is nearly room temperature. Therefore, the crystal structures of high-temperature phase with cubic symmetry might be frozen in the thin film configuration, which could be restricted by grain boundary energy. In the next section, Rietveld structural refinement of perovskite crystals in actual thin film configurations will be described.
10 Rietveld refinement of crystal structures for solar cell configuration

As described in sections 4 and 6, single-crystal XRD and neutron diffraction would be the best methods to reveal the accurate crystal structures of perovskite compounds. Although large single crystals such as 5-10 mm have been obtained for the perovskite structure analysis [159, 255], the actual microstructures of the perovskite compounds in the solar cell device configuration must be different from those of the single crystals; this is because of the various parameters including formation of microcrystals during rapid annealing, coexistence with TiO₂ layers and hole transport layers and other fabrication conditions. To understand the actual microstructures of the perovskite compounds in the device configuration, the actual cells should be measured and analyzed.

The Rietveld analysis method has been often utilized to examine the crystal structures of microcrystalline materials [256]. Nevertheless, this method has rarely been applied for crystal structures in actual perovskite solar cell devices [257]. The Rietveld refinement technique can be applied to investigate the crystal structure of the perovskite halides, and to determine the accurate atomic position and site occupancy of each atom constituting CH₃NH₃PbI₃ in the solar cell configuration [258].

Crystal structures of CH₃NH₃PbI₃ and CH₃NH₃Pb₀.₈₅Sb₀.₁₅I₃ perovskite films for the solar cell configuration were investigated and analyzed by the Rietveld analysis. This method could be also useful for the Pb-deficient perovskite compounds [259]. Using the Rietveld program RIETAN-2000 [260], a computed XRD pattern was refined to match the measured XRD pattern of the perovskite crystal in the solar cell configuration, as shown in Figure 43 [258]. Extra peaks from PbI₂, TiO₂, Au, and F-dope SnO₂ in the measured XRD patterns were excluded for the optimization process, and the charge-neutral conditions were considered and applied for the refinement.

First, the positions of MA and I ions in CH₃NH₃PbI₃ were investigated and determined. The reported basic crystal structure [134] was used to calculate the site occupancies for CH₃NH₃PbI₃, and the residual factor (R-factor, R_wp) was determined to be 3.38%. XRD profiles agreed well with the computed data by optimization of the atomic coordinates and site occupancies in the unit cell, as listed in Table 15. The refined ratio of the composition elements of the perovskite was Pb : MA : I = 1 : 1 : 3. For the Sb-added perovskite crystal, elemental concentrations of MA : Pb : Sb : I were determined to be 0.85 : 0.81 : 0.19 : 3. The reduction of MA occupancy would be due to the compensation effect by substituting Pb²⁺ with Sb³⁺, which compensates...
the deficiency of the CH$_3$NH$_3$ groups during the formation of a CH$_3$NH$_3$PbI$_3$ film [46].

Conversion efficiencies of the photovoltaic devices were improved by adding a small amount of Sb [46, 47], and these values monotonically decreased for the excess Sb concentration ($z > 0.03$). The improvement of conversion efficiencies would be due to the suppression of PbI$_2$ formation by the Sb addition, which would improve the short-circuit current density and fill factor by the electron blocking effect. Addition of Sb would also reduce the lattice constant of CH$_3$NH$_3$Pb$_{1-z}$Sb$_z$I$_3$ because of the smaller cationic radius of Sb$^{3+}$ compared to the Pb cation. The reduction of the lattice constant of the perovskite would increase the energy gap, which results in the increase of the open-circuit voltage. On the contrary, the decrease in conversion efficiencies was observed for the devices with high Sb content. From the Rietveld analysis, CH$_3$NH$_3$ vacancies were found to be introduced in the CH$_3$NH$_3$Pb$_{1-z}$Sb$_z$I$_3$, and the MA vacancies could promote the recombination of an electron and a hole. Such Rietveld refinement could be an effective method to determine the actual crystal structures for actual device configurations.

11 Conclusion

Crystal structures of various types of perovskite halide compounds possibly used for solar cells were reviewed and summarized. Structural models, XRD patterns, and electron diffraction patterns were calculated and presented to compare these structures, which could be useful for structural analysis of these types of perovskite halides by X-ray diffraction and transmission electron mi-
Table 15: Optimized crystal structures and occupancy parameters for cubic CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$Pb$_{0.81}$Sb$_{0.19}$I$_3$ in the solar cells. Copyright (2018) The Japan Society of Applied Physics.

| Atom     | Wyckoff site | x   | y   | z   | Occupancy |
|----------|--------------|-----|-----|-----|-----------|
| Pb       | 1a           | 0   | 0   | 0   | 1         |
| I        | 12h          | 0   | 0.0435 | 0.5 | 0.25      |
| N        | 12/          | 0.413 | 0.413 | 0.5 | 0.085     |
| C        | 12/          | 0.578 | 0.578 | 0.5 | 0.085     |

Cubic CH$_3$NH$_3$Pb$_{0.81}$Sb$_{0.19}$I$_3$ (space group Pm$\bar{3}$m, $a = 6.2805$ Å)

| Atom     | Wyckoff site | x   | y   | z   | Occupancy |
|----------|--------------|-----|-----|-----|-----------|
| Pb       | 1a           | 0   | 0   | 0   | 0.81      |
| Sb       | 1a           | 0   | 0   | 0   | 0.19      |
| I        | 12h          | 0   | 0.0435 | 0.5 | 0.25      |
| N        | 12/          | 0.413 | 0.413 | 0.5 | 0.071     |
| C        | 12/          | 0.578 | 0.578 | 0.5 | 0.071     |

croscopy. The stabilities of the perovskite structure could be examined by calculating the t- and $\mu$-factors, and several candidates of low-toxicity perovskite compounds can be proposed from this kind of survey. Crystal structures of the most standard CH$_3$NH$_3$PbI$_3$ and HC(NH$_2$)$_2$PbI$_3$ compounds were described in detail, especially on the arrangements of CH$_3$NH$_3$ and HC(NH$_2$)$_2$ in the crystals. In addition to the standard crystals, various types of element-substituted perovskite and double perovskite halides were described, and their XRD patterns were calculated and compared. Cation- or vacancy-ordered double perovskite compounds could be the one of the candidates for Pb-free perovskite solar cells. Low-dimensional perovskite compounds with 2-, 1-, or 0-dimensionality and 2-dimensional double perovskites were also summarized and described, which will provide the further diversity of these perovskite halides. The structural transition from tetragonal to cubic structures in the actual CH$_3$NH$_3$PbI$_3$ thin films was described, and the nanocrystals with cubic symmetry might be restricted and frozen both in and on the mesoporous TiO$_2$ layers. A very weak reflection corresponding to the tetragonal symmetry may appear, and it might be better to refer to the cubic phase as a “pseudo-cubic” phase. The perovskite layer containing dense grains with high (100)-orientation could be obtained by NH$_4$Cl addition and air blowing method. Dendritic perovskite crystals were also obtained by Br and Sb doping for FAPbI$_3$, which would be effective to control the morphology. Crystal structures of perovskite CH$_3$NH$_3$Pb$_{1-x}$Sb$_x$I$_3$ films in the actual device configuration were examined using Rietveld analysis. XRD profiles agreed well with the computed data by optimization of the atomic positions and site occupancies in the unit cell. Even for the single crystal of MAPbI$_3$, some amounts of defects such as CH$_3$NH$_3$ could exist, and the electronically neutral conditions may be maintained by the iodine defects or mixed cation valences of Pb$^{2+}$ and Pb$^{4+}$. This kind of tolerance for defects and nonstoichiometry would provide a wide processing window for these perovskite thin films. These perovskite halide crystals not only could be used for solar cells, but also could be applied for light-emitting diodes [261], laser diodes [262], catalysts [263], scintillator [264–266] and others, and the future developments of the new perovskite halide crystals are expected.

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