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 discussed to compare with 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 (CO₂). 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 CO₂, 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, CuInSe₂, dye-sensitized TiO₂, organic thin films and perovskites have been developed.

Since the first application of methylammonium lead triiodide (CH₃NH₃PbI₃) 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) [38, 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-

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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 ($\text{HC}(\text{NH}_2)_2$, FA) [27, 75–78], ethylammonium ($\text{CH}_3\text{CH}_2\text{NH}_3$, EA) [79], or guanidinium ($\text{C}(\text{NH}_2)_3$, GA) [80, 81] at the methylammonium (CH_3NH_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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ (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 $\times$ 70 mm, and an arrangement of Au electrodes on the substrate are observed [108].

An energy level diagram of the standard $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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

Figure 1: (a) Interfacial model of the perovskite solar cell. (b) Photograph of perovskite solar cell with the size of 70 mm × 70 mm. (c) Energy level diagram of the cell. Copyright (2014) The Japan Society of Applied Physics.

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

Figure 2: (a) XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films before and after annealing. Enlarged XRD patterns at a 2θ of (b) $\sim 14^\circ$ and (c) $\sim 28^\circ$. Copyright (2014) The Japan Society of Applied Physics.

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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite crystals provide structural 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ compound and the partial desorption of CH_3NH_3^+ to form PbI_2 during annealing. It should be careful that the structural transformation pre-

sented 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$, 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 $\sim 23.5^\circ$ 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 method 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 $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals are also observed as indicated by blue arrows and a rectangle.

Figure 3(c) is a high-resolution structural image of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal. CH_3NH_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 $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$. “P” in the diffraction pattern indicates $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite phase. Copyright (2014) The Japan Society of Applied Physics. (c) High-resolution TEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

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 $CH_3NH_3PbI_3$ crystal, A^+ is $CH_3NH_3^+$, B^{2+} is Pb^{2+} , and X^- is I^- . For actual application for solar cells, the basic $CH_3NH_3PbI_3$ 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 issue [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:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

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 $CH_3NH_3^+$ (MA^+), $HC(NH_2)_2^+$ (FA^+), $CH_3CH_2NH_3^+$ (EA^+), and $C(NH_2)_3^+$ (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 [μ] [142, 143, 148]. The octahedral factor (μ) can be expressed as

$$\mu = \frac{r_B}{r_X} \quad (2)$$

The t - and μ -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 μ increases from 0.414 to 0.592, 7-coordinated octahedra would be more suitable [149], and μ 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.

Figure 5: The t - and μ -factors of ABX_3 perovskite compounds.

The t - and μ -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 μ -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 μ -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 μ -factors can be computed by assuming that ions have rigid spheres and that the ionic radii are constant. However, the t - and μ -factors are a simple and helpful guideline to estimate the structural stability of the perovskite halides, and a new tolerance factor was also pro-

posed [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 $CH_3NH_3PbI_3$

$CH_3NH_3PbI_3$ is the most standard and widely used compounds for perovskite solar cells. Although the crystal structure of the $CH_3NH_3PbI_3$ has been investigated in detail, there are still some vague regions, and several structural models are proposed.

The $CH_3NH_3PbI_3$ 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 1: The t - and μ -factors of RbBX_3 , CsBX_3 , MABX_3 , FABX_3 , and GABX_3 .

Compound	t	μ	Compound	t	μ	Compound	t	μ	Compound	t	μ	Compound	t	μ
RbPbI₃	0.818	0.541	CsPbI₃	0.851	0.541	MAPbI₃	0.912	0.541	FAPbI₃	0.987	0.541	GAPbI₃	1.039	0.541
RbPbBr ₃	0.826	0.607	CsPbBr ₃	0.862	0.607	MAPbBr ₃	0.927	0.607	FAPbBr ₃	1.008	0.607	GAPbBr ₃	1.064	0.607
RbPbCl ₃	0.832	0.657	CsPbCl ₃	0.870	0.657	MAPbCl ₃	0.938	0.657	FAPbCl ₃	1.023	0.657	GAPbCl ₃	1.082	0.657
RbSnI ₃	0.886	0.423	CsSnI ₃	0.922	0.423	MASnI ₃	0.987	0.423	FASnI ₃	1.069	0.423	GASnI ₃	1.125	0.423
RbSnBr₃	0.900	0.474	CsSnBr₃	0.940	0.474	MASnBr₃	1.011	0.474	FASnBr₃	1.099	0.474	GASnBr₃	1.160	0.474
RbSnCl₃	0.911	0.514	CsSnCl₃	0.952	0.514	MASnCl₃	1.027	0.514	FASnCl₃	1.120	0.514	GASnCl₃	1.185	0.514
RbGeI ₃	0.946	0.332	CsGeI ₃	0.985	0.332	MAGeI ₃	1.055	0.332	FAGeI ₃	1.142	0.332	GAGeI ₃	1.202	0.332
RbGeBr ₃	0.967	0.372	CsGeBr ₃	1.009	0.372	MAGeBr ₃	1.086	0.372	FAGeBr ₃	1.180	0.372	GAGeBr ₃	1.246	0.372
RbGeCl ₃	0.983	0.403	CsGeCl ₃	1.027	0.403	MAGeCl ₃	1.108	0.403	FAGeCl ₃	1.208	0.403	GAGeCl ₃	1.278	0.403
RbHgI₃	0.818	0.541	CsHgI₃	0.851	0.541	MAHgI₃	0.912	0.541	FAHgI₃	0.987	0.541	GAHgI₃	1.039	0.541
RbHgBr ₃	0.826	0.607	CsHgBr ₃	0.862	0.607	MAHgBr ₃	0.927	0.607	FAHgBr ₃	1.008	0.607	GAHgBr ₃	1.064	0.607
RbHgCl ₃	0.832	0.657	CsHgCl ₃	0.870	0.657	MAHgCl ₃	0.938	0.657	FAHgCl ₃	1.023	0.657	GAHgCl ₃	1.082	0.657
RbCdI ₃	0.880	0.432	CsCdI ₃	0.916	0.432	MACdI ₃	0.981	0.432	FACdI ₃	1.062	0.432	GACdI ₃	1.118	0.432
RbCdBr₃	0.894	0.485	CsCdBr₃	0.933	0.485	MACdBr₃	1.004	0.485	FACdBr₃	1.091	0.485	GACdBr₃	1.152	0.485
RbCdCl₃	0.904	0.525	CsCdCl₃	0.945	0.525	MACdCl₃	1.020	0.525	FACdCl₃	1.112	0.525	GACdCl₃	1.176	0.525
RbZnI ₃	0.943	0.336	CsZnI ₃	0.981	0.336	MAZnI ₃	1.051	0.336	FAZnI ₃	1.138	0.336	GAZnI ₃	1.198	0.336
RbZnBr ₃	0.964	0.378	CsZnBr ₃	1.006	0.378	MAZnBr ₃	1.082	0.378	FAZnBr ₃	1.176	0.378	GAZnBr ₃	1.241	0.378
RbZnCl ₃	0.979	0.409	CsZnCl ₃	1.023	0.409	MAZnCl ₃	1.104	0.409	FAZnCl ₃	1.203	0.409	GAZnCl ₃	1.273	0.409
RbBaI ₃	0.779	0.618	CsBaI ₃	0.810	0.618	MABaI ₃	0.868	0.618	FABaI ₃	0.939	0.618	GABaI ₃	0.989	0.618
RbBaBr ₃	0.784	0.694	CsBaBr ₃	0.818	0.694	MABaBr ₃	0.880	0.694	FABaBr ₃	0.956	0.694	GABaBr ₃	1.010	0.694
RbBaCl ₃	0.787	0.751	CsBaCl ₃	0.823	0.751	MABaCl ₃	0.888	0.751	FABaCl ₃	0.968	0.751	GABaCl ₃	1.024	0.751
RbSrI₃	0.820	0.536	CsSrI₃	0.854	0.536	MASrI₃	0.914	0.536	FASrI₃	0.990	0.536	GASrI₃	1.042	0.536
RbSrBr ₃	0.829	0.602	CsSrBr ₃	0.865	0.602	MASrBr ₃	0.930	0.602	FASrBr ₃	1.011	0.602	GASrBr ₃	1.067	0.602
RbSrCl ₃	0.835	0.652	CsSrCl ₃	0.873	0.652	MASrCl ₃	0.941	0.652	FASrCl ₃	1.026	0.652	GASrCl ₃	1.085	0.652
RbCaI₃	0.866	0.455	CsCaI₃	0.902	0.455	MACaI₃	0.966	0.455	FACaI₃	1.045	0.455	GACaI₃	1.100	0.455
RbCaBr₃	0.879	0.510	CsCaBr₃	0.917	0.510	MACaBr₃	0.987	0.510	FACaBr₃	1.073	0.510	GACaBr₃	1.132	0.510
RbCaCl₃	0.888	0.552	CsCaCl₃	0.929	0.552	MACaCl₃	1.002	0.552	FACaCl₃	1.092	0.552	GACaCl₃	1.155	0.552
RbMgI ₃	0.949	0.327	CsMgI ₃	0.988	0.327	MAMgI ₃	1.058	0.327	FAMgI ₃	1.145	0.327	GAMgI ₃	1.206	0.327
RbMgBr ₃	0.971	0.367	CsMgBr ₃	1.013	0.367	MAMgBr ₃	1.090	0.367	FAMgBr ₃	1.185	0.367	GAMgBr ₃	1.251	0.367
RbMgCl ₃	0.987	0.398	CsMgCl ₃	1.031	0.398	MAMgCl ₃	1.112	0.398	FAMgCl ₃	1.213	0.398	GAMgCl ₃	1.283	0.398
RbBeI ₃	1.046	0.205	CsBeI ₃	1.089	0.205	MABeI ₃	1.166	0.205	FABeI ₃	1.262	0.205	GABeI ₃	1.329	0.205
RbBeBr ₃	1.080	0.230	CsBeBr ₃	1.127	0.230	MABeBr ₃	1.212	0.230	FABeBr ₃	1.317	0.230	GABeBr ₃	1.391	0.230
RbBeCl ₃	1.104	0.249	CsBeCl ₃	1.155	0.249	MABeCl ₃	1.245	0.249	FABeCl ₃	1.358	0.249	GABeCl ₃	1.436	0.249
RbScI ₃	0.941	0.339	CsScI ₃	0.980	0.339	MAScI ₃	1.049	0.339	FAScI ₃	1.136	0.339	GAScI ₃	1.196	0.339
RbScBr ₃	0.962	0.380	CsScBr ₃	1.004	0.380	MAScBr ₃	1.080	0.380	FAScBr ₃	1.174	0.380	GAScBr ₃	1.239	0.380
RbScCl ₃	0.977	0.412	CsScCl ₃	1.021	0.412	MAScCl ₃	1.101	0.412	FAScCl ₃	1.201	0.412	GAScCl ₃	1.270	0.412
RbTiI ₃	0.906	0.391	CsTiI ₃	0.943	0.391	MATiI ₃	1.010	0.391	FATiI ₃	1.093	0.391	GATiI ₃	1.151	0.391
RbTiBr ₃	0.923	0.439	CsTiBr ₃	0.963	0.439	MATiBr ₃	1.036	0.439	FATiBr ₃	1.126	0.439	GATiBr ₃	1.189	0.439
RbTiCl₃	0.935	0.475	CsTiCl₃	0.977	0.475	MATiCl₃	1.054	0.475	FATiCl₃	1.149	0.475	GATiCl₃	1.216	0.475
RbVI ₃	0.927	0.359	CsVI ₃	0.965	0.359	MAVI ₃	1.033	0.359	FAVI ₃	1.119	0.359	GAVI ₃	1.178	0.359
RbVBr ₃	0.946	0.403	CsVBr ₃	0.987	0.403	MAVBr ₃	1.062	0.403	FAVBr ₃	1.155	0.403	GAVBr ₃	1.219	0.403
RbVCl ₃	0.960	0.436	CsVCl ₃	1.004	0.436	MAVCl ₃	1.082	0.436	FAVCl ₃	1.180	0.436	GAVCl ₃	1.248	0.436
RbCrI ₃	0.924	0.364	CsCrI ₃	0.962	0.364	MACrI ₃	1.030	0.364	FACrI ₃	1.115	0.364	GACrI ₃	1.174	0.364
RbCrBr ₃	0.943	0.408	CsCrBr ₃	0.984	0.408	MACrBr ₃	1.058	0.408	FACrBr ₃	1.150	0.408	GACrBr ₃	1.214	0.408
RbCrCl₃	0.956	0.442	CsCrCl₃	1.000	0.442	MACrCl₃	1.078	0.442	FACrCl₃	1.176	0.442	GACrCl₃	1.244	0.442
RbMnI ₃	0.915	0.377	CsMnI ₃	0.952	0.377	MAMnI ₃	1.020	0.377	FAMnI ₃	1.104	0.377	GAMnI ₃	1.162	0.377
RbMnBr ₃	0.933	0.423	CsMnBr ₃	0.973	0.423	MAMnBr ₃	1.047	0.423	FAMnBr ₃	1.138	0.423	GAMnBr ₃	1.201	0.423
RbMnCl₃	0.945	0.459	CsMnCl₃	0.988	0.459	MAMnCl₃	1.066	0.459	FAMnCl₃	1.162	0.459	GAMnCl₃	1.229	0.459
RbFeI ₃	0.930	0.355	CsFeI ₃	0.968	0.355	MAFeI ₃	1.037	0.355	FAFeI ₃	1.122	0.355	GAFeI ₃	1.182	0.355
RbFeBr ₃	0.950	0.398	CsFeBr ₃	0.991	0.398	MAFeBr ₃	1.066	0.398	FAFeBr ₃	1.159	0.398	GAFeBr ₃	1.223	0.398
RbFeCl ₃	0.964	0.431	CsFeCl ₃	1.007	0.431	MAFeCl ₃	1.087	0.431	FAFeCl ₃	1.185	0.431	GAFeCl ₃	1.253	0.431
RbCoI ₃	0.941	0.339	CsCoI ₃	0.980	0.339	MACoI ₃	1.049	0.339	FACoI ₃	1.136	0.339	GACoI ₃	1.196	0.339
RbCoBr ₃	0.962	0.380	CsCoBr ₃	1.004	0.380	MACoBr ₃	1.080	0.380	FACoBr ₃	1.174	0.380	GACoBr ₃	1.239	0.380
RbCoCl ₃	0.977	0.412	CsCoCl ₃	1.021	0.412	MACoCl ₃	1.101	0.412	FACoCl ₃	1.201	0.412	GACoCl ₃	1.270	0.412
RbNiI ₃	0.959	0.314	CsNiI ₃	0.998	0.314	MANiI ₃	1.069	0.314	FANiI ₃	1.157	0.314	GANiI ₃	1.218	0.314
RbNiBr ₃	0.982	0.352	CsNiBr ₃	1.025	0.352	MANiBr ₃	1.102	0.352	FANiBr ₃	1.198	0.352	GANiBr ₃	1.265	0.352
RbNiCl ₃	0.998	0.381	CsNiCl ₃	1.044	0.381	MANiCl ₃	1.126	0.381	FANiCl ₃	1.228	0.381	GANiCl ₃	1.298	0.381
RbCuI ₃	0.946	0.332	CsCuI ₃	0.985	0.332	MACuI ₃	1.055	0.332	FACuI ₃	1.142	0.332	GACuI ₃	1.202	0.332
RbCuBr ₃	0.967	0.372	CsCuBr ₃	1.009	0.372	MACuBr ₃	1.086	0.372	FACuBr ₃	1.180	0.372	GACuBr ₃	1.246	0.372
RbCuCl ₃	0.983	0.403	CsCuCl ₃	1.027	0.403	MACuCl ₃	1.108	0.403	FACuCl ₃	1.208	0.403	GACuCl ₃	1.278	0.403

Table 2: Crystal systems and transition temperatures of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Reference	134	135	136
Crystal system (structure type)	Cubic (α)	Cubic (α)	Cubic (α)
Transition temperature (K)	330	327	330
Crystal system (structure type)	Tetragonal (β)	Tetragonal (β)	Tetragonal (β)
Transition temperature (K)	161	165	160
Crystal system (structure type)	Orthorhombic (γ)	Orthorhombic (γ)	Orthorhombic (γ)

Detailed crystal systems and lattice constants of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are summarized and listed in Table 3. Several structural models as the α - $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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)

Table 3: Reported crystal systems and lattice constants of $\text{CH}_3\text{NH}_3\text{PbI}_3$. SCND: single crystal neutron diffraction, NPD: neutron powder diffraction, SCXRD: single crystal X-ray diffraction.

Structure type	Crystal system	Space group	Lattice constant (Å)	V (Å ³)	Z	V/Z (Å ³)	Analysis method	Temperature (K)	Reference
α	Cubic	$Pm\bar{3}m$	$a = 6.315(3)$	251.8	1	251.8	SCND	350	159
α	Cubic	$Pm\bar{3}m$	$a = 6.31728(27)$	252.1	1	252.1	NPD	352	160
α	Cubic	$Pm\bar{3}m$	$a = 6.391(1)$	261.0	1	261.0	SCXRD	338	134
α	Tetragonal (Pseudo-cubic)	$P4mm$	$a = 6.3115(2),$ $c = 6.3161(2)$	251.6	1	251.6	SCXRD	400	161
β	Tetragonal	$I4/mcm$	$a = 8.8796(6),$ $c = 12.6266(18)$	995.6	4	248.9	SCND	295	159
β	Tetragonal	$I4cm$	$a = 8.849(2),$ $c = 12.642(2)$	990.0	4	247.5	SCXRD	293	161
β	Tetragonal	$I4/mcm$	$a = 8.800(9),$ $c = 12.685(7)$	982.3	4	245.6	SCXRD	220	158
β	Tetragonal	$I4/mcm$	$a = 8.80625(28),$ $c = 12.7127(5)$	985.9	4	246.5	NPD	180	160
γ	Orthorhombic	$pnma$	$a = 8.86574(30),$ $b = 12.6293(4),$ $c = 8.57689(31)$	960.3	4	240.0	NPD	100	160
γ	Orthorhombic	$pnma$	$a = 8.8362(11),$ $b = 12.5804(15),$ $c = 8.5551(10)$	951.0	4	237.8	SCXRD	100	118
γ	Orthorhombic	$pnma$	$a = 8.8155(4),$ $b = 12.5980(6),$ $c = 8.5637(5)$	951.1	4	237.8	NPD	4	135

ion (CH_3NH_3^+) has polarity and C_{3v} point group symmetry, which could provide a pseudo-cubic structure [161]. As described in section 2, the pseudo-cubic has nearly cubic symmetry with an a/c ratio of ~ 1 . The CH_3NH_3^+ is arranged along the C_2 axis with 12 equivalent orientations in the unit cell. Hydrogen (H) atoms of the CH_3NH_3^+ provide two structural configurations on the C_2 axis. Accordingly, the degrees of freedom of the MA^+ ion are 24 [157]. The entropy changes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were also measured to be $19.0 \text{ J K}^{-1} \text{ mol}^{-1}$ (161.4 K) and $9.7 \text{ J K}^{-1} \text{ mol}^{-1}$ (330.4 K), and the transition entropies indicates that the phase transitions are due to the order-disorder transition [157]. The methylammonium 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 CH_3NH_3^+ , 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 CH_3NH_3^+ and deviations of stoichiometry could exist at the crystal surface even for the single crystal of $\text{CH}_3\text{NH}_3\text{PbI}_3$, the electronic charge deviation may be compensated by introducing the iodine defects or deviations of the mixed cation valences of Pb^{2+} and Pb^{4+} , 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.

Figure 6: Structural models of cubic or pseudo-cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ corresponding to reported models in (a) [134], (b) [161], (c) [160], and (d) [159]. (e) Atomic displacement parameter ellipsoids shown at 50% probability of model (d).

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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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_3NH_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_3NH_3^+ cations for the [110], [100], and [111] directions were 0.670:0.187:0.143 [159], respectively, which indicates that the CH_3NH_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_3NH_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 Wyck-off 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$. For space group $Pm\bar{3}m$ (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} (Å ²)
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 $\text{CH}_3\text{NH}_3\text{PbI}_3$. 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} (Å ²)
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 $\text{CH}_3\text{NH}_3\text{PbI}_3$. CH_3NH_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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ structure transforms into the orthorhombic $\text{CH}_3\text{NH}_3\text{PbI}_3$ structure, which is caused by the molecular ordering of the CH_3NH_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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 ~ 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)

Figure 10: Calculated X-ray diffraction patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ with cubic, tetragonal and orthorhombic structures.

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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ are shown in Figure 10, and the Miller indices, diffraction angles, d -spacings, and relative intensities of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal.

Calculated XRD patterns of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$. 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$. Equivalent indices were combined. For space group $Pm\bar{3}m$ (221), $a = 6.315(3)$ Å at 350 K.

Index	2θ (°)	d -spacing (Å)	Relative intensity (%)	Multiplicity
1 0 0	14.0124	6.3150	100	6
1 1 0	19.8665	4.4654	8	12
1 1 1	24.3935	3.6460	6	8
2 0 0	28.2399	3.1575	50	6
2 1 0	31.6557	2.8242	48	24
2 1 1	34.7687	2.5781	5	24
2 2 0	40.3638	2.2327	27	12
2 2 1	42.9296	2.1050	17	24
3 0 0	42.9296	2.1050	4	6
3 1 0	45.3773	1.9970	3	24
3 1 1	47.7259	1.9040	1	24
2 2 2	49.9899	1.8230	7	8
3 2 0	52.1812	1.7515	8	24
3 2 1	54.3093	1.6878	3	48
4 0 0	58.4060	1.5788	3	6

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

Index	2θ (°)	d -spacing (Å)	Relative intensity (%)	Multiplicity
0 0 2	14.0162	6.3133	53	2
1 1 0	14.0935	6.2788	100	4
1 1 2	19.9271	4.4519	7	8
2 0 0	19.9821	4.4398	7	4
2 1 1	23.4646	3.7881	15	16
2 0 2	24.4909	3.6317	12	8
0 0 4	28.2477	3.1567	33	2
2 2 0	28.4060	3.1394	54	4
2 1 3	30.9339	2.8884	6	16
1 1 4	31.7002	2.8203	29	8
2 2 2	31.8072	2.8110	22	8
3 1 0	31.8429	2.8080	35	8
2 0 4	34.8441	2.5727	4	8
3 1 2	34.9427	2.5656	8	16
3 2 1	37.1645	2.4172	2	16
2 2 4	40.4910	2.2260	34	8
4 0 0	40.6065	2.2199	13	4
2 1 5	42.3817	2.1309	2	16
3 2 3	42.4930	2.1256	1	16
4 1 1	42.5486	2.1230	7	16
0 0 6	42.9417	2.1044	2	2
3 1 4	43.0794	2.0980	27	16
4 0 2	43.1618	2.0942	7	8
3 3 0	43.1893	2.0929	2	4
4 2 0	45.6535	1.9855	3	8
4 1 3	47.378	1.9172	4	16
4 0 4	50.2002	1.8158	12	8
3 2 5	51.8101	1.7631	1	16
4 3 1	51.9534	1.7586	2	16
2 2 6	52.2914	1.7480	3	8
3 3 4	52.4100	1.7444	3	8
5 1 0	52.5048	1.7414	4	8
3 1 6	54.4407	1.6840	2	16
4 2 4	54.5560	1.6807	4	16
5 1 2	54.6252	1.6787	1	16
4 1 5	56.0777	1.6387	2	16
4 3 3	56.1682	1.6362	1	16
0 0 8	58.4233	1.5783	2	2
4 4 0	58.7754	1.5697	2	4
1 1 8	60.4265	1.5307	4	8

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

Table 8: Calculated crystal parameters of CH₃NH₃PbI₃.

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	<i>pnma</i>	$a = 8.850, b = 12.688, c = 8.564$	961.6	4	240.4	VASP	10	136

Figure 12: Structural models of cubic CH₃NH₃PbI₃ observed along (a) [100], (b) [110], (c) [111], and (d) [210].

bined peak due to the small crystallite size could mislead the results from the XRD structural analysis, and one should be very careful of that.

Computed crystal parameters of the CH₃NH₃PbI₃ 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 CH₃NH₃⁺.

5 Electron diffraction of cubic and tetragonal CH₃NH₃PbI₃

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 CH₃NH₃PbI₃

Figure 13: Calculated electron diffraction patterns of cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ along (a) [100], (b) [110], (c) [111], and (d) [210].

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

observed along the [100], [110], [111], and [210] directions. It should be noted that the mean positions of CH_3NH_3 sites are shown in the projected structural models. The resultant electron diffraction patterns of the cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ computed along these four different directions are shown in Figure 13. Clear reflections with 6-fold symmetry are observed along [111], as shown in Figure 13(c).

Figure 14 is structural models of the tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ tilted along the [001], [100], [021], and [221]

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

directions, which correspond to [100], [110], [111], and [210], respectively, of the cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ in Figure 12. For the tetragonal phase, deviations of the iodine site are decreased, and the mean positions of CH_3NH_3 are shown in the projected model. The resultant electron diffraction patterns of the tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ projected along the [210] (Figure 13(d)) and the tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{HC}(\text{NH}_2)_2\text{PbI}_3$

In addition to the most standard $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite compound, $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ and mixed $\text{MAPbI}_3/\text{FAPbI}_3$ perovskite compounds are also widely used and studied. The structural models of the $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ crystals are summarized and shown in Figure 16. High photoconversion efficiencies were reported for $\alpha\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ with a cubic structure [167, 168], which is a stable black phase at room temperature, as shown in Figure 16(a). When the $\alpha\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ crystal is cooled below ~ 200 K, the α -phase is transformed to $\beta\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ with a trigonal structure, as shown in Figure 16(b) and 16(c). On the other hand, the $\alpha\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ phase is converted to the $\delta\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ 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 $\text{HC}(\text{NH}_2)_2^+$ cations.

Figure 16: Structural models of (a) $\alpha\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ along [100], $\beta\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ along (b) [001] and (c) [112], and (d) $\delta\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ along [001].

Local arrangements of the trigonal planar $\text{HC}(\text{NH}_2)_2^+$ cations in the unit cell were determined by neutron diffraction [167], as shown in Figure 17. The $\text{HC}(\text{NH}_2)_2^+$ cation exists at the central mirror plane of the cube, and the $\text{HC}(\text{NH}_2)_2^+$ 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 NH_2 group interact with the iodide ions of PbI_3^- [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 MAPbI_3 observed in Figure 6(e).

Calculated XRD patterns of α -, β -, and $\delta\text{-HC}(\text{NH}_2)_2\text{PbI}_3$ crystals with cubic, trigonal, and hexagonal structures [161] are shown in Figure 18, and computed XRD parameters of the cubic and hexagonal FAPbI_3 are summarized and listed in Tables 9 and 10, respectively. In the cubic $\alpha\text{-FAPbI}_3$ phase, site occupancies of C–H and N–H are 1/6 and 1/12, respectively. For the $\delta\text{-FAPbI}_3$, the occupancies were set at 2/3 for N and 1 for C. The 100 reflection position at lower 2θ angles is characteristic of the $\delta\text{-FAPbI}_3$ phase [161], and can be applied for distinction between the α - and δ -phases. Several small reflections appear in the diffraction pattern for the $\beta\text{-FAPbI}_3$, which

Table 9: Calculated X-ray diffraction parameters of cubic $\alpha\text{-HC}(\text{NH}_2)_2\text{PbI}_3$. Equivalent indices were combined. For space group $Pm\bar{3}m$ (221), $a = 6.3620(8)$ Å at 298 K.

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 $\text{HC(NH}_2)_2\text{PbI}_3$. (c) Atomic displacement parameter ellipsoids shown at 50% probability of (a).

Figure 18: Calculated X-ray diffraction patterns of α -, β -, and δ - $\text{HC(NH}_2)_2\text{PbI}_3$.

Table 10: Calculated X-ray diffraction parameters of hexagonal δ - $\text{HC(NH}_2)_2\text{PbI}_3$. Equivalent indices were combined. For space group $P6_3mc$ (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	3.4957	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

is due to the symmetry reduction of the cubic α -FAPbI₃ phase to the trigonal β -phase with lower crystal symmetry.

7 Elemental substituted perovskites and double perovskites

In previous sections, two most standard crystal structures of CH₃NH₃PbI₃ and HC(NH₂)₂PbI₃ were described. In addition to these standard MAPbI₃ and FAPbI₃ halide perovskites, elemental substitution is possible for ABX₃ 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 MAPbI₃ and FAPbI₃ 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 CH₃NH₃PbBr₃ and CH₃NH₃PbCl₃ in Figure 19, indicating the effect of halogen substitution. When the Br[−] ions are substituted by Cl[−] ions, the diffraction peaks of CH₃NH₃PbCl₃ are shifted to higher angles compared with those of CH₃NH₃PbBr₃. Furthermore, when Pb²⁺ ions are substituted by Sn²⁺ ions, the diffraction intensities of CH₃NH₃SnCl₃ fairly change compared with those of CH₃NH₃PbCl₃. CH₃NH₃⁺ ions can also be substituted by Cs⁺ ions, as shown in the structural models of CsSnI₃ and CsPbBr₃ in Figure 20(a) and 20(b), respectively.

Calculated XRD patterns of HC(NH₂)₂SnI₃, CH₃NH₃SnI₃, and CsSnI₃ are shown in Figure 21, which indicate the A site substitutions in the ABX₃ perovskite. The diffraction pattern of MASnI₃ is similar to that of FASnI₃, whereas the diffraction peak intensities of CsSnI₃ are fairly different from those of the MASnI₃ and FASnI₃, 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 CH₃NH₃PbBr₃, CH₃NH₃PbCl₃ and CH₃NH₃SnCl₃ with cubic structures.

Figure 20: Structural models of (a) CsSnI₃ and (b) CsPbBr₃.

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	$Pm\bar{3}m$	$a = 5.933(2)$	1	298	134
	Tetragonal	$I4/mcm$	$a = 8.3381(3), c = 11.8587(5)$	4	220	169
	Tetragonal	$P4/mmm$	$a = 5.894(2), c = 5.861(2)$	1	150-155	156
	Orthorhombic	$Pna2_1$	$a = 7.979(1), b = 8.580(2), c = 11.849(2)$	4	< 145	156
CH ₃ NH ₃ PbCl ₃	Cubic	$Pm\bar{3}m$	$a = 5.666(2)$	1	200	134
	Tetragonal	$P4/mmm$	$a = 5.656, c = 5.630$	2	173-179	156
	Orthorhombic	$P222_1$	$a = 5.673, b = 5.628, c = 11.182$	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	$Pm\bar{3}m$	$a = 5.6917(2)$	1	475	170
	Rhombohedral	$R3m$	$a = 5.6784(1), \alpha = 90.945(1)^\circ$	1	370	170
	Orthorhombic	$Pnma$	$a = 11.1567(1), b = 7.3601(1), c = 8.2936(1)$	4	250	170
	Monoclinic	$P2_1/n$	$a = 10.9973(1), b = 7.22043(1), c = 8.2911(1), \alpha = 90.470(1)^\circ$	4	2	170
CH ₃ NH ₃ SnCl ₃	Cubic	$Pm\bar{3}m$	$a = 5.760(1)$	1	478	171
	Rhombohedral	$R3m$	$a = 5.734(1), \alpha = 91.90(1)^\circ$	1	350	171
	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 ₂) ₂ PbI ₃	Trigonal	$P3$	$a = 17.7914(8), c = 10.9016(6)$	12	150	161
HC(NH ₂) ₂ PbBr ₃	Cubic	$Pm\bar{3}m$	$a = 5.98618(2)$	1	275	172
	Tetragonal	$P4/mbm$	$a = 8.41525(5), c = 5.94735(8)$	2	175	172
	Orthorhombic	$Pnma$	$a = 8.37433(9), b = 11.8609(1), c = 8.38073(9)$	4	100	172
HC(NH ₂) ₂ SnI ₃	Cubic	$Pm\bar{3}m$	$a = 6.30961(1)$	1	275	172
	Tetragonal	$P4/mbm$	$a = 8.86227(2), c = 6.24892(2)$	2	175	172
	Orthorhombic	$Pnma$	$a = 8.81749(8), b = 12.41641(7), c = 8.8578(1)$	4	100	172
HC(NH ₂) ₂ SnI ₃	Orthorhombic	$Amm2$	$a = 6.3286(10), b = 8.9554(11), c = 8.9463(11)$	2	340	161
CsPbI ₃	Orthorhombic	$Pnma$	$a = 8.8561(4), b = 8.5766(3), c = 12.4722(6)$	4	293	173
CsPbBr ₃	Cubic	$Pm\bar{3}m$	$a = 5.874$	1	433	174
CsSnI ₃	Cubic	$Pm\bar{3}m$	$a = 6.2057(7)$	1	500	175
	Tetragonal	$P4/mbm$	$a = 8.7182(8), c = 6.1908(6)$	2	380	175
	Orthorhombic	$Pnma$	$a = 8.6885(5), b = 12.3773(4), c = 8.6384(6)$	4	300	175
CsSnBr ₃	Cubic	$Pm\bar{3}m$	$a = 5.80$	1	298	176
CsSnCl ₃	Cubic	$Pm\bar{3}m$	$a = 5.604(1)$	1	413	171
CsGeI ₃	Cubic	$Pm\bar{3}m$	$a = 6.05(1)$	1	573	177
CsGeBr ₃	Cubic	$Pm\bar{3}m$	$a = 5.69(1)$	1	543	177
RbGeI ₃	Cubic	$Pm\bar{3}m$	$a = 5.994(3)$	1	533	178
RbGeBr ₃	Cubic	$Pm\bar{3}m$	$a = 5.659(2)$	1	538	179

Lattice constants of several perovskite halide compounds with the ABX₃ 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 ABX₃ 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 A₂BB'X₆, and the ionic valence of B/B' is 1⁺/3⁺ or 2⁺/2⁺. One of the examples of the double perovskite structure is Cs₂AgBiBr₆, and

the structural models observed along the [100], [110], and [111] crystal directions are shown in Figure 23(a), (b), and (c), respectively. AgBr₆ and BiBr₆ octahedra are alternately ordered in the perovskite crystal, as shown in Figure 23(b) and 23(d).

Various double perovskite halide compounds such as Cs₂AgInCl₆, Cs₂NaBiCl₆, Cs₂KEuCl₆, Cs₂LiScCl₆, (CH₃NH₃)₂AgBiBr₆, (CH₃NH₃)₂KBiCl₆, Rb₂NaCrCl₆, and others have been reported, as listed in Table 12, which are all Pb-free compounds. Calculated X-ray diffraction patterns of Cs₂AgInCl₆, Cs₂AgBiCl₆, and Cs₂AgBiBr₆ are

Table 12: Crystal systems of various double perovskite halide compounds.

Compound	Crystal system	Space group	Lattice parameters (Å)	Z	Temperature (K)	Reference
Cs ₂ AgBiBr ₆	Cubic	$Fm\bar{3}m$	$a = 11.2499$	4	300	182
Cs ₂ AgBiCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.7774(2)$	4	-	183
Cs ₂ AgInCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.48059(5)$	4	300	184
Cs ₂ NaBiCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.8429(1)$	4	RT	185
(CH ₃ NH ₃) ₂ AgBiBr ₆	Cubic	$Fm\bar{3}m$	$a = 11.6370(1)$	4	300	186
(CH ₃ NH ₃) ₂ KBiCl ₆	Rhombohedral	$R\bar{3}m$	$a = 7.8372(2), c = 20.9938(2)$	3	300	187
Cs ₂ NaHoCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.722$	4	294	188
Cs ₂ NaYCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.7275(2)$	4	294	188
Cs ₂ NaCeCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.943(2)$	4	-	189
Cs ₂ NaErCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.7089$	4	-	190
Cs ₂ NaSmCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.8342$	4	-	190
Cs ₂ NaYBr ₆	Cubic	$Fm\bar{3}m$	$a = 11.3047(6)$	4	-	191
Cs ₂ LiInCl ₆	Rhombohedral	$R\bar{3}m$	$a = 7.3184(4), c = 36.240(3)$	6	-	191
Cs ₂ LiLuCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.409$	4	-	192
Cs ₂ LiScCl ₆	Rhombohedral	$R\bar{3}m$	$a = 7.2965(6), c = 35.989(4)$	6	-	191
Cs ₂ LiYCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.4857(5)$	4	-	191
Cs ₂ KBiCl ₆	Cubic	$Fm\bar{3}m$	$a = 11.086(5)$	4	293	193
Cs ₂ KCrCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.633(2)$	4	-	194
Cs ₂ KEuCl ₆	Cubic	$Fm\bar{3}m$	$a = 11.1633(3)$	4	296	195
Cs ₂ KLaCl ₆	Cubic	$Fm\bar{3}m$	$a = 11.379(5)$	4	-	196
Cs ₂ KScCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.873(3)$	4	-	192
Cs ₂ KYCl ₆	Cubic	$Fm\bar{3}m$	$a = 11.128(5)$	4	-	196
Rb ₂ LiDyBr ₆	Tetragonal	$I4/mmm$	$a = 7.699(5), c = 11.032(6)$	2	293	197
Rb ₂ NaCrCl ₆	Cubic	$Fm\bar{3}m$	$a = 10.131(2)$	4	-	194
Rb ₂ NaTmCl ₆	Tetragonal	$P4/nbm$	$a = 10.530(4), c = 10.599(4)$	4	295	198

Figure 21: Calculated X-ray diffraction patterns of HC(NH₂)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 $\text{Cs}_2\text{AgBiBr}_6$ 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 $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{AgBiCl}_6$, and $\text{Cs}_2\text{AgBiBr}_6$ double perovskites.

MA^+ ions can be substituted at the Cs site, and structural models of $\text{MA}_2\text{KBiCl}_6$ 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 $\text{Cs}_2\text{NaBiCl}_6$, $(\text{CH}_3\text{NH}_3)_2\text{KBiCl}_6$, and $(\text{CH}_3\text{NH}_3)_2\text{AgBiBr}_6$ are shown in Figure 26. If the Cs^+ ions are substituted by the MA^+ ions,

Figure 25: Structural models of $(\text{CH}_3\text{NH}_3)_2\text{KBiCl}_6$ double perovskite structures observed along (a) [001] and (b) [100].

Figure 26: Calculated X-ray diffraction patterns of $\text{Cs}_2\text{NaBiCl}_6$, $(\text{CH}_3\text{NH}_3)_2\text{KBiCl}_6$, and $(\text{CH}_3\text{NH}_3)_2\text{AgBiBr}_6$.

the diffraction peaks of $\text{MA}_2\text{AgBiBr}_6$ are shifted to lower angles compared with those of $\text{Cs}_2\text{NaBiCl}_6$, and the diffraction intensities fairly change. Since the $\text{MA}_2\text{KBiCl}_6$ 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 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_2SnCl_6 compound in Figure 27, there are insufficient Sn atoms to form $RbSn_{0.5}Cl_3$, 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_2BvX_6 , where the v means vacant positions corresponding to the B' site for the $A_2BB'X_6$ double

perovskites. Despite the isolated octahedral BX_6 units, the close-packed iodide lattice provides electronic dispersion, and Cs_2SnI_6 and other perovskites were applied to solar cells [237, 238]. Pb free solar cells such as $FA_4GeSbCl_{12}$ have been reported [239], in which the double elements were selected to replace Pb. $Cs_2TiI_xBr_{6-x}$ 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_4PbBr_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_2SnCl_6 with 0-dimensional perovskite structures, observed along (a) [100], (b) [110], and (c) [111]. (d) Perspective view of the structure.

Figure 28: Structural models of Cs_4PbBr_6 with 0-dimensional perovskite structures, observed along (a) [001], (b) [100], and (c) [210]. (d) Perspective view of the structure.

Figure 29: Structural models of $Cs_3Sb_2I_9$ with 0-dimensional biocuboctahedra structures, observed along (a) [001] and (b) [100].

Table 13: Crystal systems of low-dimensional perovskite crystals.

Compound	Dimensionality	Crystal system	Space group	Lattice parameters (Å) and degrees	Z	Reference
$C_6N_2H_{16}PbI_4$	2	Monoclinic	Pc	$a = 10.4999(13)$, $b = 12.5429(9)$, $c = 12.5289(13)$, $\beta = 89.984(9)^\circ$	4	208
$(C_6N_2H_{16})(CH_3NH_3)Pb_2I_7$	2	Monoclinic	Cc	$a = 23.1333(7)$, $b = 8.8365(3)$, $c = 8.8354(3)$, $\beta = 90^\circ$	4	208
$(C_6N_2H_{16})(CH_3NH_3)_3Pb_4I_{13}$	2	Monoclinic	Cc	$a = 8.8587(18)$, $b = 8.8571(18)$, $c = 58.915(12)$, $\beta = 90^\circ$	4	208
$(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)Pb_2I_7$	2	Orthorhombic	$Cmcm$	$a = 8.9470(4)$, $b = 39.347(2)$, $c = 8.8589(6)$	4	209
$(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_2Pb_3I_{10}$	2	Orthorhombic	$Aba2$	$a = 8.9275(6)$, $b = 51.959(4)$, $c = 8.8777(6)$	4	209
$(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_3Pb_4I_{13}$	2	Orthorhombic	$Ama2$	$a = 8.9274(4)$, $b = 64.383(4)$, $c = 8.8816(4)$	4	209
$(CH_3NH_3)_2CuCl_4$	2	Monoclinic	$P2_1/c$	$a = 7.2574(8)$, $b = 7.3504(1)$, $c = 9.9688(5)$, $\beta = 111.20^\circ$	1	210
$(CH_3NH_3)_2CuCl_2Br_2$	2	Orthorhombic	$Cmca$	$a = 7.3194(4)$, $b = 7.3281(4)$, $c = 19.1344(1)$	2	210
$(C_6H_5(CH_2)_2NH_3)_2CdCl_4$	2	Orthorhombic	$Aba2$	$a = 7.4444(2)$, $b = 38.8965(3)$, $c = 7.3737(2)$	4	211
$(CH_3(CH_2)_2NH_3)_4AgInCl_8$	2 + double perovskite	Triclinic	$P\bar{1}$	$a = 7.454(3)$, $b = 7.866(3)$, $c = 24.629(8)$, $\alpha = 90.141(10)^\circ$, $\beta = 89.992(10)^\circ$, $\gamma = 90.049(11)^\circ$	2	212
$(CH_3(CH_2)_2NH_3)_4AgInBr_8$	2 + double perovskite	Monoclinic	$C2/m$	$a = 24.5633(13)$, $b = 7.7838(4)$, $c = 8.2501(4)$, $\beta = 90.091(2)^\circ$	2	212
$(CH_3(CH_2)_2NH_3)_4AgBiBr_8$	2 + double perovskite	Monoclinic	$C2/m$	$a = 24.503(7)$, $b = 7.964(2)$, $c = 8.384(2)$, $\beta = 90.045(9)^\circ$	2	212
$(NH_3(CH_2)_4NH_3)_2AgBiBr_8$	2 + double perovskite	Triclinic	$P\bar{1}$	$a = 8.1018(3)$, $b = 8.2433(3)$, $c = 9.6813(4)$, $\alpha = 101.1960(10)^\circ$, $\beta = 92.055(2)^\circ$, $\gamma = 90.3960(10)^\circ$	1	212
$(CH_3(CH_2)_7NH_3)_4AgBiBr_8$	2 + double perovskite	Monoclinic	$P2_1/m$	$a = 8.2024(7)$, $b = 8.1797(6)$, $c = 21.1217(18)$, $\beta = 101.195(3)^\circ$	1	212
$(CH_3(CH_2)_2NH_3)_2CsAgBiBr_7$	2 + double perovskite	Monoclinic	$P2_1/m$	$a = 8.053(4)$, $b = 7.997(3)$, $c = 18.536(8)$, $\beta = 102.503(11)^\circ$	2	212
α - $Cs_3Sb_2Cl_9$	2	Trigonal	$P321$	$a = 7.633$, $c = 9.345$	1	213
β - $Cs_3Sb_2Cl_9$	1	Orthorhombic	$Pnma$	$a = 7.630(20)$, $b = 13.079(3)$, $c = 18.663(4)$	1	214
$CsTiI_3$	1	Hexagonal	$P6_3/mmc$	$a = 8.214(2)$, $c = 6.789(2)$	2	215
$CsTiBr_3$	1	Hexagonal	$P6_3/mmc$	$a = 7.656(1)$, $c = 6.357(1)$	2	216
$CsTiCl_3$	1	Hexagonal	$P6_3/mmc$	$a = 7.3086(7)$, $c = 6.0670(8)$	2	217
$C_{24}H_{35}S_8N_4PbI_5$	1	Monoclinic	$P2_1/c$	$a = 17.553(2)$, $b = 8.710(1)$, $c = 27.122(5)$, $\beta = 97.57(2)^\circ$	4	218
Cs_2SnI_6	0	Cubic	$Fm\bar{3}m$	$a = 11.6276(9)$	4	161
Cs_2SnBr_6	0	Cubic	$Fm\bar{3}m$	$a = 10.7435(2)$	4	219
Cs_2SnCl_6	0	Cubic	$Fm\bar{3}m$	$a = 10.3552(2)$	4	220
Cs_4PbBr_6	0	Trigonal	$R\bar{3}c$	$a = 13.7219(2)$, $c = 17.3153(3)$	6	221
Cs_4PbCl_6	0	Trigonal	$R\bar{3}c$	$a = 13.182(5)$, $c = 16.641(5)$	6	222
Cs_2TiI_6	0	Cubic	$Fm\bar{3}m$	$a = 11.473(3)$	4	223
Cs_2TiCl_6	0	Cubic	$Fm\bar{3}m$	$a = 10.23$	4	224
Cs_2TeI_6	0	Cubic	$Fm\bar{3}m$	$a = 11.7088(1)$	4	225
Rb_2SnI_6	0	Cubic	$Fm\bar{3}m$	$a = 8.07056(6)$, $c = 11.76501(1)$	4	226
Rb_2SnCl_6	0	Cubic	$Fm\bar{3}m$	$a = 10.137(2)$	4	227
$(NH_4)_2PtI_6$	0	Cubic	$Fm\bar{3}m$	$a = 11.158(8)$	4	228
K_2PtCl_6	0	Cubic	$Fm\bar{3}m$	$a = 9.743(3)$	4	229
$Cs_3Sb_2I_9$	0-dimer	Hexagonal	$P6_3/mmc$	$a = 8.349(1)$, $c = 20.916(1)$	2	230
$Cs_3Bi_2I_9$	0-dimer	Monoclinic	$C2/c$	$a = 8.346(6)$, $b = 14.472(9)$, $c = 21.10(1)$, $\beta = 91.00(6)^\circ$	4	231

pound is $\text{Cs}_3\text{Sb}_2\text{I}_9$, which satisfies the charge neutral condition. The faces of two SbI_6 octahedra are connected to each other, and the SbI_6 dimers or biotetrahedra are isolated in the crystal.

Figure 30: Calculated X-ray diffraction patterns of Cs_4PbBr_6 , Rb_2SnCl_6 , and $\text{Cs}_3\text{Sb}_2\text{I}_9$.

Figure 31: Structural models of CsTiCl_3 with 1-dimensional continuous perovskite structures, observed along (a) [001] and (b) [100]. (c) Perspective view of the structure.

Calculated XRD patterns of Cs_4PbBr_6 , Rb_2SnCl_6 , and $\text{Cs}_3\text{Sb}_2\text{I}_9$, with trigonal, cubic, and hexagonal symmetries, respectively, are shown in Figure 30. For the Rb_2SnCl_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 $Fm\bar{3}m$. However, the reflection intensities are different from those of common double perovskite, which is due to the vacant B' site for the $\text{A}_2\text{BB}'\text{X}_6$ double perovskite structure. Diffraction patterns of Cs_4PbBr_6 and $\text{Cs}_3\text{Sb}_2\text{I}_9$ are fairly different from that of Rb_2SnCl_6 , and a 002 reflection appears at a 2θ of 8.4° (not shown in Figure 30) for the $\text{Cs}_3\text{Sb}_2\text{I}_9$ 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: Structural models of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ with 1-dimensional perovskite structures, observed along (a) [100], (b) [010], and (c) [001].

Figure 32 is a structural model of orthorhombic β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ 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 - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ 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

Figure 33: Structural models of (a) α - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and (b) $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ with 2-dimensional perovskite structures. H atoms are omitted in (b).

$\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ were also synthesized as Pb-free light harvesters [241, 242], as shown in Figure 33(b).

XRD patterns of the 2D α - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$, 1D β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$, 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 $\text{A}(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$. $\text{C}_6\text{N}_2\text{H}_{16}\text{PbI}_4$, $(\text{C}_6\text{N}_2\text{H}_{16})(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{I}_7$, and $(\text{C}_6\text{N}_2\text{H}_{16})(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}$ 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 $\text{C}_6\text{N}_2\text{H}_{16}\text{PbI}_4$, $(\text{C}_6\text{N}_2\text{H}_{16})(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{I}_7$, and $(\text{C}_6\text{N}_2\text{H}_{16})(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}$ 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.

Figure 34: Calculated X-ray diffraction patterns of α - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$, β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$, and CsTiCl_3 .

Figure 35: Structural models of (a) $C_6N_2H_{16}PbI_4$, (b) $(C_6N_2H_{16})(CH_3NH_3)Pb_2I_7$, and (c) $(C_6N_2H_{16})(CH_3NH_3)_3Pb_4I_{13}$ 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 $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ ($n = 1, 2, 3, 4, \infty$). The perovskite iodides of $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)Pb_2I_7$ ($n = 2$), $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_2Pb_3I_{10}$ ($n = 3$), and $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_3Pb_4I_{13}$ ($n = 4$) 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-butyldiammonium (BDA) into standard 3D double perovskites [212]. Figure 38(a,b), (c), (d), and 38(e) show structural models of $(NH_3(CH_2)_4NH_3)_2$

Figure 36: Calculated X-ray diffraction patterns of $C_6N_2H_{16}PbI_4$, $(C_6N_2H_{16})(CH_3NH_3)Pb_2I_7$, and $(C_6N_2H_{16})(CH_3NH_3)_3Pb_4I_{13}$ with 2-dimensional perovskite structures.

$AgBiBr_8$ ($BDA_2AgBiBr_8$), $(CH_3(CH_2)_7NH_3)_4AgBiBr_8$ ($OCA_4AgBiBr_8$), $(CH_3(CH_2)_2NH_3)_4AgInCl_8$ ($PA_4AgInCl_8$), and $(CH_3(CH_2)_2NH_3)_2CsAgBiBr_7$ ($PA_2CsAgBiBr_7$) with 2-dimensional double perovskite structures, respectively. The general formulas of the single-layered Ruddlesden-Popper type and single-layered Dion–Jacobson type are $A_4BB'X_8$ ($A = PA$ or OCA) and $A_2BB'X_8$, respectively. The band gap energy can be tuned by selecting the spacer layer thickness, and the band gaps of $PA_4AgBiBr_8$ and $PA_4AgInCl_8$ 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) $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{I}_7$, (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.

Figure 39: Calculated X-ray diffraction patterns of $(\text{NH}_3(\text{CH}_2)_4\text{NH}_3)_2\text{AgBiBr}_8$, $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_4\text{AgInCl}_8$, and $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2\text{CsAgBiBr}_7$ 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 TiO_2 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 (NH_4Cl) to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ solar cells fabricated by an air blowing method are described here [246]. NH_4Cl 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 $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ here.

For the perovskite layer, a mixture solution containing $\text{CH}_3\text{NH}_3\text{I}$ (190.7 mg), PbCl_2 (111.2 mg) and NH_4Cl (0–5 mg) was arranged [248–251], and the solution containing

$\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ was spin-coated on the mesoporous TiO_2 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 decaphenylcyclopentasilane is used over the perovskite layer, the annealing temperature can be raised to $\sim 200^\circ\text{C}$, and the devices show excellent stability [97].

Optical microscope (OM) images of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ 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 NH_4Cl . The particle sizes of the perovskite grains were decreased by addition of NH_4Cl 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite compound. Atomic compositions were estimated by the energy dispersive spectroscopy analysis [246], which indicates that the Cl would be doped into the $\text{CH}_3\text{NH}_3\text{PbI}_3$ compounds, as listed in Table 14.

Figures 41(a) and 41(b) show XRD patterns of the FTO/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ /spiro-OMeTAD/Au devices without or with NH_4Cl , respectively [246]. The diffraction reflections are indexed by the cubic perovskite halide. An XRD pattern of a $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ device fabricated without PbCl_2 or air blowing is also shown in Figure 41(c). All diffraction intensities due to the perovskite compound are very weaker compared with those of Figure 41(a) and 41(b), and diffraction peaks corresponding to TiO_2 and FTO are observed.

As seen in Figure 41, diffraction intensities of 100 and 200 reflections were enormously enhanced to more than 100 times by introducing NH_4Cl and air blow. The diffraction intensity ratio I_{100}/I_{210} were measured and summarized, as listed in Table 14. If the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite grains are randomly oriented, the I_{100}/I_{210} value should be 2.1, as shown in Table 14. The orientation index I_{100}/I_{210} is 61 for the cell fabricated using air blow and without NH_4Cl , which indicates that the perovskite grains are preferentially (100)-aligned against the cell substrate. The orientation index I_{100}/I_{210} was further enhanced to 3600 by the addition of NH_4Cl , which is 1700 times higher than that of randomly aligned perovskite grains. The cell fabricated with NH_4Cl and without PbCl_2 or air blow provided an orientation index I_{100}/I_{210} of 2.8, which indicates the most of the perovskite grains are randomly aligned in the thin film configuration. The orientation indices of

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 CH₃NH₃PbI₃ crystals.**No air blowing or PbCl₂. **Figure 40:** (a) Optical microscope images, SEM images and corresponding elemental mapping images of the CH₃NH₃PbI₃(Cl) cell (a) without NH₄Cl and containing 5 mg of NH₄Cl.

I_{100}/I_{FTO} are also listed in Table 14, and the I_{100}/I_{FTO} also increased by using the NH₄Cl and air blow.

Two formation mechanisms were proposed for the highly (100)-aligned perovskite thin films on the mesoporous TiO₂. 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 TiO₂. 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 NH₄Cl, 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.

Figure 41: XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells containing (a) 0 mg, (b) 5 mg of NH_4Cl , and (c) XRD pattern of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell containing 5 mg of NH_4Cl without air blowing.

Cl substitution at iodine sites also improves the carrier diffusion in the perovskite halide compounds. Excess $\text{CH}_3\text{NH}_3\text{Cl}$ is vaporized from the initial stoichiometry of $3(\text{CH}_3\text{NH}_3\text{I}) + \text{PbCl}_2$ [248–251], and a little remained Cl is substituted at the I site of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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. The present air-blowing method combined with NH_4Cl addition is an effective method to form highly crystal-aligned perovskite thin films in the device configuration.

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 $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ on the mesoporous TiO_2 and F-doped SnO_2 substrate, and the perovskite grains with dark contrast are distributed keeping their distances of $\sim 10 \mu\text{m}$ [252]. Figures 42(b), 42(c) and 42(d) are also optical microscope images of $\text{HC}(\text{NH}_2)_2\text{PbI}_{2.85}\text{Br}_{0.15}$, $\text{HC}(\text{NH}_2)_2\text{PbIBr}_2$, and

$\text{HC}(\text{NH}_2)_2\text{Pb}_{0.95}\text{Sb}_{0.05}\text{I}_3$, 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 $\text{HC}(\text{NH}_2)_2$, 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 (σ) with a vector form, and can be calculated from the following equation:

$$\Delta G_V = \frac{2E_b V_m}{D} \quad (3)$$

where ΔG_V , E_b , D , and V_m are the Gibbs free energy, grain boundary energy, grain size, and molar volume, respectively. When the $\text{CH}_3\text{NH}_3\text{PbI}_3$ decomposes into PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$, the $\Delta_r G^\circ$ was calculated to be $10.2 \text{ (kJ mol}^{-1}\text{)}$ [254]. Grain sizes of perovskite crystals observed perpendicular to the substrates are measured to be $\sim 5 \mu\text{m}$ in Figures 40 and 42, and the grain boundary energies were estimated to be $\sim 170 \text{ J m}^{-2}$. On the other hand, crystallite sizes of these thin films measured parallel to the substrates by XRD were $\sim 50 \text{ nm}$, and the grain boundary energies were estimated to be $\sim 1.7 \text{ J m}^{-2}$. 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 $\sim 330 \text{ K}$ 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.

Figure 42: Optical microscope images of (a) $\text{HC}(\text{NH}_2)_2\text{PbI}_3$, (b) $\text{HC}(\text{NH}_2)_2\text{PbI}_{2.85}\text{Br}_{0.15}$, (c) $\text{HC}(\text{NH}_2)_2\text{PbIBr}_2$, and (d) $\text{HC}(\text{NH}_2)_2\text{Pb}_{0.95}\text{Sb}_{0.05}\text{I}_3$. (e) Grain growth of the perovskite.

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 TiO_2 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the solar cell configuration [258].

Crystal structures of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{Pb}_{0.85}\text{Sb}_{0.15}\text{I}_3$ perovskite films for the solar cell conformation 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 PbI_2 , TiO_2 , Au, and F-dope SnO_2 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ were investigated and determined. The reported basic crystal structure [134] was used to calculate the site occupancies for $\text{CH}_3\text{NH}_3\text{PbI}_3$, 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 $\text{Pb} : \text{MA} : \text{I} = 1 : 1 : 3$. For the Sb-added perovskite crystal, elemental concentrations of $\text{MA} : \text{Pb} : \text{Sb} : \text{I}$ 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 Pb^{2+} with Sb^{3+} , which compensates

Figure 43: Measured (solid) and optimized (dotted) X-ray diffraction profiles for the (a) $\text{CH}_3\text{NH}_3\text{PbI}_3$ and (b) $\text{CH}_3\text{NH}_3\text{Pb}_{0.85}\text{Sb}_{0.15}\text{I}_3$ solar cells.

the deficiency of the CH_3NH_3 groups during the formation of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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 $\text{CH}_3\text{NH}_3\text{Pb}_{1-z}\text{Sb}_z\text{I}_3$ 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_3NH_3 vacan-

cies were found to be introduced in the $\text{CH}_3\text{NH}_3\text{Pb}_{1-z}\text{Sb}_z\text{I}_3$, 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{Pb}_{0.81}\text{Sb}_{0.19}\text{I}_3$ in the solar cells. Copyright (2018) The Japan Society of Applied Physics.

Cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ (space group $Pm\bar{3}m$, $a = 6.2883 \text{ \AA}$)					
Atom	Wyckoff site	x	y	z	Occupancy
Pb	1a	0	0	0	1
I	12h	0	0.0435	0.5	0.25
N	12j	0.413	0.413	0.5	0.085
C	12j	0.578	0.578	0.5	0.085
Cubic $\text{CH}_3\text{NH}_3\text{Pb}_{0.81}\text{Sb}_{0.19}\text{I}_3$ (space group $Pm\bar{3}m$, $a = 6.2805 \text{ \AA}$)					
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	12j	0.413	0.413	0.5	0.071
C	12j	0.578	0.578	0.5	0.071

croscopy. The stabilities of the perovskite structure could be examined by calculating the t - and μ -factors, and several candidates of low-toxicity perovskite compounds can be proposed from this kind of survey. Crystal structures of the most standard $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ compounds were described in detail, especially on the arrangements of CH_3NH_3 and $\text{HC}(\text{NH}_2)_2$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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_4Cl 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 $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Sb}_x\text{I}_3$ films in the actual de-

vice 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_3NH_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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References

- [1] Federici, G., C. Bachmann, L. Barucca, W. Biel, L. Boccaccini, R. Brown, et al. DEMO design activity in Europe: Progress and updates. *Fusion Engineering and Design*, Vol. 136, 2018, pp. 729–741.
- [2] Gopalaswamy, V., R. Betti, J. P. Knauer, N. Luciani, D. Patel, K. M. Woo, et al. Tripled yield in direct-drive laser fusion through statistical modelling. *Nature*, Vol. 565, No. 7741, 2019, pp. 581–586.
- [3] Entler, S., J. Horacek, T. Dlouhy, and V. Dostal. Approximation of the economy of fusion energy. *Energy*, Vol. 152, 2018, pp. 489–497.
- [4] Liu, D. G., L. Zheng, L. M. Luo, X. Zan, J. P. Song, Q. Xu, X. Y. Zhu, and Y. C. Wu. An overview of oxidation-resistant tungsten alloys for nuclear fusion. *Journal of Alloys and Compounds*, Vol. 765, 2018, pp. 299–312.
- [5] Oku, T. Possible applications of nanomaterials for nuclear fusion devices. *Energy Harvesting Systems*, Vol. 5, No. 1-2, 2018, pp. 11–27.
- [6] Oku, T. *Solar Cells and Energy Materials*. De Gruyter, Berlin, Germany, 2017. <https://doi.org/10.1515/9783110298505>
- [7] Kojima, A., K. Teshima, Y. Shirai, and T. Miyasaka. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, Vol. 131, No. 17, 2009, pp. 6050–6051.
- [8] Im, J.H., C.R. Lee, J.W. Lee, S.W. Park, and N.G. Park. 6.5% efficient perovskite quantum-dot-sensitized solar cell. *Nanoscale*, Vol. 3, 2011, pp. 4088–4093.

- [9] Lee, M. M. J. Teusch er, T. Miyasaka, T.N. Murakami, and H. J. Snaith. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*, Vol. 338, 2012, pp. 643–647.
- [10] Kim, H. S., and C. R. Lee. J.H. Im, K.B. Lee, T. Moehl, A. Marchioro, S.J. Moon, J.H. Yum, R. Humphry-Baker, and J.E. Moser. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Scientific Reports*, Vol. 2, 2012, pp. 591–597.
- [11] Kojima, A., M. Ikegami, K. Teshima, and T. Miyasaka, Highly luminescent lead bromide perovskite nanoparticles synthesized with porous alumina media. *Chemistry Letters*, Vol. 41, 2012, 397–399.
- [12] Chung, I., B. Lee, J. He, R. P. H. Chang, and M. G. Kanatzidis. All-solid-state dye-sensitized solar cells with high efficiency. *Nature*, Vol. 485, No. 7399, 2012, pp. 486–489.
- [13] Im, J.H., J. Chung, S.J. Kim, and N.G. Park, Synthesis, structure, and photovoltaic property of a nanocrystalline 2H perovskite-type novel sensitizer $(\text{CH}_3\text{CH}_2\text{NH}_3)\text{PbI}_3$. *Nanoscale Research Letters*, Vol. 7, 2012, 353–1-7.
- [14] Grinberg, I., D. V. West, M. Torres, G. Gou, D. M. Stein, L. Wu, G. Chen, and E. M. Gallo. A. A. kbashev, and P.K. Davies. Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials. *Nature*, Vol. 503, 2013, pp. 509–512.
- [15] Stranks, S. D., G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith. Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science*, Vol. 342, No. 6156, 2013, pp. 341–344.
- [16] Burschka, J., N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, Vol. 499, No. 7458, 2013, pp. 316–319.
- [17] Liu, M., M. B. Johnston, and H. J. Snaith. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature*, Vol. 501, No. 7467, 2013, pp. 395–398.
- [18] Liu, D., and T. L. Kelly. Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. *Nature Photonics*, Vol. 8, No. 2, 2014, pp. 133–138.
- [19] Wang, J. T. W., J. M. Ball, E. M. Barea, A. Abate, J. A. Alexander-Webber, J. Huang, et al. Low-Temperature Processed Electron Collection Layers of Graphene/TiO₂ Nanocomposites in Thin Film Perovskite Solar Cells. *Journal of Nanoscience Letters*, Vol. 14, No. 2, 2014, pp. 724–730.
- [20] Wojciechowski, K., M. Saliba, T. Leijtens, A. Abate, and H. J. Snaith. Sub-150°C processed meso-superstructured perovskite solar cells with enhanced efficiency. *Energy & Environmental Science*, Vol. 7, No. 3, 2014, pp. 1142–1147.
- [21] Snaith, H. J., A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, et al. Anomalous Hysteresis in Perovskite Solar Cells. *Journal of Physical Chemistry Letters*, Vol. 5, No. 9, 2014, pp. 1511–1515.
- [22] Nie, W., H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta. Solar cells. High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science*, Vol. 347, No. 6221, 2015, pp. 522–525.
- [23] Dong, Q., Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, and J. Huang. Solar cells. Electron-hole diffusion lengths > 175 μm in solution-grown $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. *Science*, Vol. 347, No. 6225, 2015, pp. 967–970.
- [24] Jeon, N.J., J.H. Noh, W.S. Yang, Y.C. Kim, S. Ryu, J. Seo, and S.I. Seok, Compositional engineering of perovskite materials for high-performance solar cells. *Nature*, Vol. 517, 2015, pp. 476–480.
- [25] Saliba, M., S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.P. Correa- Baena, et al. A molecularly engineered hole-transporting material for efficient perovskite solar cells. *Nature Energy*, 1 (2016) 15017-1-7.
- [26] Bi, D., C. Yi, J. Luo, J. D. Décoppet, F. Zhang, S. M. Zakeeruddin, et al. Polymer-templated nucleation and crystal growth of perovskite films for solar cells with efficiency greater than 21%. *Nature Energy*, Vol. 1, No. 10, 2016, p. 16142.
- [27] Bi, D., W. Tress, M.I. Dar, P. Gao, J. Luo, C. Renevier, et al. Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Science Advances*, Vol. 2, 2016, e1501170-1-7.
- [28] Saliba, M., T. Matsui, J. Y. Seo, K. Domanski, J. P. Correa-Baena, M. K. Nazeeruddin, et al. Cesium-containing triple cation perovskite solar cells: Improved stability, reproducibility and high efficiency. *Energy & Environmental Science*, Vol. 9, No. 6, 2016, pp. 1989–1997.
- [29] Saliba, M., T. Matsui, K. Domanski, J. Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, et al. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science*, Vol. 354, No. 6309, 2016, pp. 206–209.
- [30] He, M., B. Li, X. Cui, B. Jiang, Y. He, Y. Chen, et al. Meniscus-assisted solution printing of large-grained perovskite films for high-efficiency solar cells. *Nature Communications*, Vol. 8, 2017, 16045-1-10.
- [31] Shin, S. S., E. J. Yeom, W. S. Yang, S. Hur, M. G. Kim, J. Im, et al. Colloidally prepared La-doped BaSnO_3 electrodes for efficient, photostable perovskite solar cells. *Science*, Vol. 356, No. 6334, 2017, pp. 167–171.
- [32] Wang, J. M., Z. K. Wang, M. Li, C. C. Zhang, L. L. Jiang, K. H. Hu, et al. Doped copper phthalocyanine via an aqueous solution process for normal and inverted perovskite solar cells. *Advanced Energy Materials*, Vol. 7, 2017, 1701688-1-8.
- [33] Arora, N., M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin, and M. Grätzel. Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. *Science*, Vol. 358, No. 6364, 2017, pp. 768–771.
- [34] Yang, W. S., B. W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, et al. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science*, Vol. 356, No. 6345, 2017, pp. 1376–1379.
- [35] Cho, Y., A. M. Soufiani, J. S. Yun, J. Kim, D. S. Lee, J. Seidel, et al. Mixed 3D-2D passivation treatment for mixed-cation lead mixed-halide perovskite solar cells for higher efficiency and better stability. *Advanced Energy Materials*, Vol. 8, 2018, 1703392-1-10.
- [36] Zhao, Y., H. Tan, H. Yuan, Z. Yang, J. Z. Fan, J. Kim, et al., Perovskite seeding growth of formamidinium-lead-iodide-based perovskites for efficient and stable solar cells. *Nature Communications*, Vol. 9, 2018, 1607-1-10.
- [37] Tang, Z., T. Bessho, F. Awai, T. Kinoshita, M. M. Maitani, R. Jono, et al., Hysteresis-free perovskite solar cells made of potassium-doped organometal halide perovskite. *Scientific Reports*, Vol. 7, 2017, 12183-1-7.
- [38] Xu, W., L. Zheng, X. Zhang, Y. Cao, T. Meng, D. Wu, et al. Efficient perovskite solar cells fabricated by Co partially substituted hybrid perovskite. *Advanced Energy Materials*, 15 (2018) 1703178-1-11.

- [39] Oku, T. *Solar Cells – New Approaches and Reviews*, Kosyachenko, L. A., Ed., InTech, Rijeka, Croatia, 2015, Chapter 3, pp. 77–102.
- [40] Oku, T., M. Zushi, K. Suzuki, Y. Ohishi, T. Matsumoto, and A. Suzuki. *Nanostructured Solar Cells*, Das, N., Ed., InTech, Rijeka, Croatia, 2017, Chapter 11, pp. 217–243.
- [41] Hao, F., C. C. Stoumpos, D. H. Cao, R. P. H. Chang, and M. G. Kanatzidis. Lead-free solid-state organic–inorganic halide perovskite solar cells. *Nature Photonics*, Vol. 8, No. 6, 2014, pp. 489–494.
- [42] Zuo, F., S. T. Williams, P. W. Liang, C. C. Chueh, C. Y. Liao, and A. K. Y. Jen. Binary-metal perovskites toward high-performance planar-heterojunction hybrid solar cells. *Advanced Materials*, Vol. 26, No. 37, 2014, pp. 6454–6460.
- [43] Liao, W., D. Zhao, Y. Yu, N. Shrestha, K. Ghimire, C. R. Grice, C. Wanget al. Fabrication of efficient low-bandgap perovskite solar cells by combining formamidinium tin iodide with methylammonium lead iodide. *Journal of the American Chemical Society*, Vol. 138, No. 38, 2016, pp. 12360–12363.
- [44] Zhu, H. L., J. Xiao, J. Mao, H. Zhang, Y. Zhao, and W.C.H. Choy, Controllable crystallization of $\text{CH}_3\text{NH}_3\text{Sn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites for hysteresis-free solar cells with efficiency reaching 15.2%. *Advanced Functional Materials*, Vol. 27, 2017, 1605469-1-8.
- [45] Tavakoli, M. M., S. M. Zakeeruddin, M. Grätzel, and Z. Fan, Large-grain tin-rich perovskite films for efficient solar cells via metal alloying technique. *Advanced Materials*, Vol. 30, 2018, 1705998-1-9.
- [46] Oku, T., Y. Ohishi, and A. Suzuki. Effects of antimony addition to perovskite-type $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices. *Chemistry Letters*, Vol. 45, No. 2, 2016, pp. 134–136.
- [47] Zhang, J., M. H. Shang, P. Wang, X. Huang, J. Xu, Z. Hu, et al. n-type doping and energy states tuning in $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Sb}_{2x/3}\text{I}_3$ perovskite solar cells. *ACS Energy Letters*, Vol. 1, No. 3, 2016, pp. 535–541.
- [48] Yamanouchi, J., T. Oku, Y. Ohishi, M. Fukaya, N. Ueoka, H. Tanaka, and A. Suzuki. Fabrication and characterization of perovskite $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Sb}_x\text{I}_{3-3x}\text{Br}_3$ photovoltaic device. *Advanced Materials Research*, Vol. 7, 2018, pp. 435–446.
- [49] Jahandar, M., J. H. Heo, C. E. Song, K. J. Kong, W. S. Shi, J. C. Lee, et al. Highly efficient metal halide substituted $\text{CH}_3\text{NH}_3\text{I}(\text{PbI}_2)_{1-x}(\text{CuBr}_2)_x$ planar perovskite solar cells. *Nano Energy*, Vol. 27, 2016, pp. 330–339.
- [50] Abdi-Jalebi, M., M. I. Dar, A. Sadhanala, S. P. Senanayak, M. Franckevičius, N. Arora, et al., Impact of Monovalent Cation Halide Additives on the Structural and Optoelectronic Properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite. *Advanced Energy Materials*, 6 (2016) 1502472-1-10.
- [51] Shirahata, Y., and T. Oku, Effects of copper addition on photovoltaic properties of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ solar cells. *Physica Status Solidi A*, Vol. 214, 2017, 1700268-1-6.
- [52] Shirahata, Y. and T. Oku. Microstructures, optical and photovoltaic properties of $\text{CH}_3\text{NH}_3\text{PbI}_{3(1-x)}\text{Cl}_x$ perovskite films with CuSCN additive. *Materials Research Express*, Vol. 5, No. 5, 2018, 055504-1–10.
- [53] Tanaka, H., Y. Ohishi, and T. Oku. Effects of Cu addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ photovoltaic devices with hot airflow during spin-coating. *Japanese Journal of Applied Physics*, Vol. 57, 2018, 08RE10-1–5.
- [54] Tanaka, H., T. Oku, and N. Ueoka. Fabrication and Characterization of the copper bromides-added $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite solar cells. *Synthetic Metals*, Vol. 244, 2018, pp. 128–133.
- [55] Ueoka, N., T. Oku, and A. Suzuki. Additive effects of alkali metals on Cu-modified $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ photovoltaic devices. *RSC Advances*, Vol. 9, No. 42, 2019, pp. 24231–24240.
- [56] Hamatani, T., and T. Oku. Effects of halide addition to arsenic-doped perovskite photovoltaic devices. *AIP Conference Proceedings*, Vol. 1929, 2018, 020018-1–8.
- [57] Krishnamoorthy, T., H. Ding, C. Yan, W. L. Leong, T. Baikie, Z. Zhang, et al. Lead-free germanium iodide perovskite materials for photovoltaic applications. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 3, No. 47, 2015, pp. 23829–23832.
- [58] Ohishi, Y., T. Oku, and A. Suzuki. Fabrication and characterization of perovskite-based $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Ge}_x\text{I}_3$, $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Tl}_x\text{I}_3$ and $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{In}_x\text{I}_3$ photovoltaic devices. *AIP Conference Proceedings*, Vol. 1709, 2016, 020020-1–8.
- [59] Tanaka, H., Y. Ohishi, and T. Oku. Effects of GeI_2 or ZnI_2 addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices. *AIP Conference Proceedings*, Vol. 1929, 2018, 020007-1–7.
- [60] Zhao, W., D. Yang, Z. Yang, and S. Liu. Zn-doping for reduced hysteresis and improved performance of methylammonium lead iodide perovskite hybrid solar cells. *Materials Today Energy*, Vol. 5, 2017, pp. 205–213.
- [61] Shai, X., J. Wang, P. Sun, W. Huang, P. Liao, F. Cheng et al. Achieving ordered and stable binary metal perovskite via strain engineering. *Nano Energy*, Vol. 48, 2018, pp. 117–127.
- [62] Zheng, H., G. Liu, X. Xu, A. Alsaedi, T. Hayat, X. Pan, and S. Dai. Acquiring high-performance and stable mixed-dimensional perovskite solar cells by using a transition-metal-substituted Pb precursor. *ChemSusChem*, Vol. 11, No. 18, 2018, pp. 3269–3275.
- [63] Zhang, X., J. Yin, Z. Nie, Q. Zhang, N. Sui, B. Chen, et al. Lead-free and amorphous organic–inorganic hybrid materials for photovoltaic applications: Mesoscopic $\text{CH}_3\text{NH}_3\text{MnI}_3/\text{TiO}_2$ heterojunction. *RSC Advances*, Vol. 7, No. 59, 2017, pp. 37419–37425.
- [64] Taguchi, M., A. Suzuki, H. Tanaka, and T. Oku. Fabrication and characterization of perovskite solar cells added with MnCl_2 , YCl_3 or poly(methyl methacrylate). *AIP Conference Proceedings*, Vol. 1929, 2018, 020012-1–8.
- [65] Zhang, H., H. Wang, S. T. Williams, D. Xiong, W. Zhang, C. C. Chueh, et al., SrCl_2 derived perovskite facilitating a high efficiency of 16% in hole-conductor-free fully printable mesoscopic perovskite solar cells. *Advanced Materials*, Vol. 29, 2017, 1606608-1-8.
- [66] Klug, M. T., A. Osherov, A. A. Haghighirad, S. D. Stranks, P. R. Brown, S. Bai, et al. Tailoring metal halide perovskites through metal substitution: Influence on photovoltaic and material properties. *Energy & Environmental Science*, Vol. 10, No. 1, 2017, pp. 236–246.
- [67] Wang, L., H. Zhou, J. Hu, B. Huang, M. Sun, B. Dong, et al. A Eu^{3+} - Eu^{2+} ion redox shuttle imparts operational durability to PbI_3 perovskite solar cells. *Science*, Vol. 363, No. 6424, 2019, pp. 265–270.
- [68] Park, B. W., B. Philippe, X. Zhang, H. Rensmo, G. Boschloo, and E. M. J. Johansson. Bismuth based hybrid perovskites A_3BiI_9 (A: methylammonium or cesium) for solar cell application. *Advanced Materials*, Vol. 27, No. 43, 2015, pp. 6806–6813.
- [69] Suárez, I., M. Vallés-Pelarda, A. F. Gualdrón-Reyes, I. Mora-Seró, A. Ferrando, H. Michinel. Outstanding nonlinear optical properties of methylammonium- and Cs-PbX_3 ($\text{X} = \text{Br}, \text{I}$, and Br-I) perovskites: Polycrystalline thin films and nanoparticles. *APL Materials*, Vol. 7, No. 4, 2019, 041106-1–9.

- [70] Ueoka, N., T. Oku, A. Suzuki, H. Sakamoto, M. Yamada, S. Minami, and S. Miyauchi. Fabrication and characterization of $\text{CH}_3\text{NH}_3(\text{Cs})\text{Pb}(\text{Sn})\text{I}_3(\text{Cl})$ perovskite solar cells with TiO_2 nanoparticle layers. *Japanese Journal of Applied Physics*, Vol. 57, No. 7, 2018, 02CE03-1-7.
- [71] Turren-Cruz, S. H., M. Saliba, M. T. Mayer, H. Juárez-Santisteban, X. Mathew, L. Nienhaus, et al. Enhanced charge carrier mobility and lifetime suppress hysteresis and improve efficiency in planar perovskite solar cells. *Energy & Environmental Science*, Vol. 11, No. 1, 2018, pp. 78–86.
- [72] Jung, M. H., S. H. Rhim, and D. Moon. $\text{TiO}_2/\text{RbPbI}_3$ halide perovskite solar cells. *Solar Energy Materials and Solar Cells*, Vol. 172, 2017, pp. 44–54.
- [73] Zhao, W., Z. Yao, F. Yu, D. Yang, and S. Liu. Alkali metal doping for improved $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells. *Advanced Science*, Vol. 5, 2018, 1700131-1-7.
- [74] Machiba, H., T. Oku, T. Kishimoto, N. Ueoka, and A. Suzuki. Fabrication and evaluation of K-doped $\text{MA}_{0.8}\text{FA}_{0.1}\text{K}_{0.1}\text{PbI}_3(\text{Cl})$ perovskite solar cells. *Chemical Physics Letters*, Vol. 730, 2019, pp. 117–123.
- [75] Yang, W. S., J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo, and S. I. Seok. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, Vol. 348, No. 6240, 2015, pp. 1234–1237.
- [76] Zhou, Y., M. Yang, S. Pang, K. Zhu, and N. P. Padture. Exceptional morphology-preserving evolution of formamidinium lead triiodide perovskite thin films via organic-cation displacement. *Journal of the American Chemical Society*, Vol. 138, No. 17, 2016, pp. 5535–5538.
- [77] Hu, M., L. Liu, A. Mei, Y. Yang, T. Liu, and H. Han. Efficient hole-conductor-free, fully printable mesoscopic perovskite solar cells with a broad light harvester $\text{NH}_2\text{CH}=\text{NH}_2\text{PbI}_3$. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 2, No. 40, 2014, pp. 17115–17121.
- [78] Suzuki, A., M. Kato, N. Ueoka, and T. Oku. Additive effect of formamidinium chloride in methylammonium lead halide compound-based perovskite solar cells. *Journal of Electronic Materials*, Vol. 48, No. 6, 2019, pp. 3900–3907.
- [79] Peng, W., X. Miao, V. Adinolfi, E. Alarousu, O. E. Tall, A. H. Emwas, et al. Engineering of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite crystals by alloying large organic cations for enhanced thermal stability and transport properties. *Angewandte Chemie International Edition*, Vol. 55, No. 36, 2016, pp. 10686–10690.
- [80] Jodowski, A. D., C. Roldán-Carmona, G. Grancini, M. Salado, M. Ralaifarisoa, S. Ahmad, et al. Large guanidinium cation mixed with methylammonium in lead iodide perovskites for 19% efficient solar cells. *Nature Energy*, Vol. 2, No. 12, 2017, pp. 972–979.
- [81] Kishimoto, T., A. Suzuki, N. Ueoka, and T. Oku. Effects of guanidinium addition to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite photovoltaic devices. *Journal of the Ceramic Society of Japan*, Vol. 127, No. 7, 2019, pp. 491–497.
- [82] Shi, D., V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, et al. Solar cells. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science*, Vol. 347, No. 6221, 2015, pp. 519–522.
- [83] He, J., and T. Chen. Additive regulated crystallization and film formation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ for highly efficient planar-heterojunction solar cells. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 3, No. 36, 2015, pp. 18514–18520.
- [84] Zhou, H., Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, et al. Photovoltaics. Interface engineering of highly efficient perovskite solar cells. *Science*, Vol. 345, No. 6196, 2014, pp. 542–546.
- [85] Wehrenfennig, C., M. Liu, H. J. Snaith, M. B. Johnston, and L. M. Herz. Charge-carrier dynamics in vapour-deposited films of the organolead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. *Energy & Environmental Science*, Vol. 7, No. 7, 2014, pp. 2269–2275.
- [86] Xie, F. X., H. Su, J. Mao, K. S. Wong, and W. C. H. Choy. Evolution of diffusion length and trap state induced by chloride in perovskite solar cell. *Journal of Physical Chemistry C*, Vol. 120, No. 38, 2016, pp. 21248–21253.
- [87] Oku, T., K. Suzuki, and A. Suzuki. Effects of chlorine addition to perovskite-type $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices. *Journal of the Ceramic Society of Japan*, Vol. 124, No. 3, 2016, pp. 234–238.
- [88] Wang, F., A. Shimazaki, F. Yang, K. Kanahashi, K. Matsuki, Y. Miyauchi, et al. Highly efficient and stable perovskite solar cells by interfacial engineering using solution-processed polymer layer. *Journal of Physical Chemistry C*, Vol. 121, No. 3, 2017, pp. 1562–1568.
- [89] Li, G., T. Zhang, F. Xu, and Y. Zhao. A facile deposition of large grain and phase pure $\alpha\text{-FAPbI}_3$ for perovskite solar cells via a flash crystallization. *Materials Today Energy*, Vol. 5, 2017, pp. 293–298.
- [90] Taguchi, M., A. Suzuki, N. Ueoka, and T. Oku. Effects of poly(methyl methacrylate) addition to perovskite photovoltaic devices. *AIP Conference Proceedings*, Vol. 2067, 2019, 020018-1-8.
- [91] Guo, J. J., Z. C. Bai, X. F. Meng, M. M. Sun, J. H. Song, Z. S. Shen, et al. Novel dopant-free metallophthalocyanines based hole transporting materials for perovskite solar cells: The effect of core metal on photovoltaic performance. *Solar Energy*, Vol. 155, 2017, pp. 121–129.
- [92] Jiang, X., Z. Yu, H. B. Li, Y. Zhao, J. Qu, J. Lai, et al. A solution-processable copper(ii) phthalocyanine derivative as a dopant-free hole-transporting material for efficient and stable carbon counter electrode-based perovskite solar cells. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 5, No. 34, 2017, pp. 17862–17866.
- [93] Wang, J. M., Z. K. Wang, M. Li, C. C. Zhang, L. L. Jiang, K. H. Hu, et al. Doped copper phthalocyanine via an aqueous solution process for normal and inverted perovskite solar cells. *Advanced Energy Materials*, Vol. 8, 2018, 1701688-1-8.
- [94] Suzuki, A., H. Okumura, Y. Yamasaki, and T. Oku. Fabrication and characterization of perovskite type solar cells using phthalocyanine complexes. *Applied Surface Science*, Vol. 488, 2019, pp. 586–592.
- [95] Oku, T., J. Nomura, A. Suzuki, H. Tanaka, S. Fukunishi, S. Minami, and S. Tsukada. Fabrication and characterization of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells added with polysilanes. *International Journal of Photoenergy*, Vol. 2018, 2018, 8654963-1-7.
- [96] Taguchi, M., A. Suzuki, T. Oku, S. Fukunishi, S. Minami, and M. Okita. Effects of decaphenylcyclopentasilane addition on photovoltaic properties of perovskite solar cells. *Coatings*, Vol. 8, 2018, 461-1-10.
- [97] Taguchi, M., A. Suzuki, T. Oku, N. Ueoka, S. Minami, and M. Okita. Effects of annealing temperature on decaphenylcyclopentasilane-inserted $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells. *Chemical Physics Letters*, Vol. 737, 2019, 136822-1-7.
- [98] Guo, Y., Q. Wang, and W. A. Saidi. Structural stabilities and electronic properties of high-angle grain boundaries in perovskite

- cesium lead halides. *Journal of Physical Chemistry C*, Vol. 121, No. 3, 2017, pp. 1715–1722.
- [99] Lee, J. W., S. H. Bae, N. D. Marco, Y. H. Hsieh, Z. Dai, and Y. Yang. The role of grain boundaries in perovskite solar cells. *Materials Today Energy*, Vol. 7, 2018, pp. 149–160.
- [100] Zhou, W., Z. Wen, and P. Gao. Less is more: dopant-free hole transporting materials for high-efficiency perovskite solar cells. *Advanced Energy Materials*, Vol. 8, 2018, 1702512-1-28.
- [101] Wang, C., H. Hao, S. Chen, K. Cao, H. Yu, Q. Zhang, et al., Inverse-architecture perovskite solar cells with 5,6,11,12-tetraphenylanthracene as a hole conductor. *RSC Advances*, Vol. 7, 2017, pp. 29944–29952.
- [102] Zhang, H., H. Wang, W. Chen, and A. K. Y. Jen. CuGaO_2 : A promising inorganic hole-transporting material for highly efficient and stable perovskite solar cells. *Advanced Materials*, Vol. 29, No. 8, 2017, pp. 1604984-1-8.
- [103] Suzuki, A., T. Kida, T. Takagi, and T. Oku. Effects of hole-transporting layers of perovskite-based solar cells. *Japanese Journal of Applied Physics*, Vol. 55, 2016, 02BF01-1–5.
- [104] Yang, G., H. Tao, P. Qin, W. Ke, and G. Fang. Recent progress in electron transport layers for efficient perovskite solar cells. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 4, No. 11, 2016, pp. 3970–3990.
- [105] Chen, B. X., H. S. Rao, W. G. Li, Y. F. Xu, H. Y. Chen, D. B. Kuang, and C. Y. Su. Achieving high-performance planar perovskite solar cell with Nb-doped TiO_2 compact layer by enhanced electron injection and efficient charge extraction. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 4, No. 15, 2016, pp. 5647–5653.
- [106] Oku, T., T. Iwata, and A. Suzuki. Effects of niobium addition into TiO_2 layers on $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based photovoltaic devices. *Chemistry Letters*, Vol. 44, No. 7, 2015, pp. 1033–1035.
- [107] Chen, W., Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, et al. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science*, Vol. 350, No. 6263, 2015, pp. 944–948.
- [108] Oku, T., T. Matsumoto, A. Suzuki, and K. Suzuki. Fabrication and characterization of a perovskite-type solar cell with a substrate size of 70 mm. *Coatings*, Vol. 5, No. 4, 2015, pp. 646–655.
- [109] Li, X., D. Bi, C. Yi, J. D. Décoppet, J. Luo, S. M. Zakeeruddin, et al. A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells. *Science*, Vol. 353, No. 6294, 2016, pp. 58–62.
- [110] Higuchi, H., and T. Negami. Largest highly efficient $203 \times 203 \text{ mm}^2$ $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar modules. *Japanese Journal of Applied Physics*, Vol. 57, 8S3, 2018, 08RE11-1–6.
- [111] Zhou, Y., M. Yang, A. L. Vasiliev, H. F. Garces, Y. Zhao, D. Wang, et al. Growth control of compact $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films via enhanced solid-state precursor reaction for efficient planar perovskite solar cells. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 3, No. 17, 2015, pp. 9249–9256.
- [112] Zong, Y., Y. Zhou, M. Ju, H. F. Garces, A. R. Krause, F. Ji et al. Thin-film transformation of NH_4PbI_3 to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite: A methylamine-induced conversion-healing process. *Angewandte Chemie International Edition*, Vol. 55, No. 47, 2016, pp. 14723–14727.
- [113] Oku, T., M. Kanayama, Y. Ono, T. Akiyama, Y. Kanamori, and M. Murozon. Microstructures, optical and photoelectric conversion properties of spherical silicon solar cells with anti-reflection $\text{SnO}_x\text{:F}$ thin films. *Japanese Journal of Applied Physics*, Vol. 53, 2014, 05FJ03-1–7.
- [114] Oku, T., S. Hori, A. Suzuki, T. Akiyama, and Y. Yamasaki. Fabrication and characterization of PCBM:P3HT:silicon phthalocyanine bulk heterojunction solar cells with inverted structures. *Japanese Journal of Applied Physics*, Vol. 53, 2014, 05FJ08-1–5.
- [115] Oku, T. *Structure Analysis of Advanced Nanomaterials*. De Gruyter, Berlin, Germany, 2014. <https://doi.org/10.1515/9783110305012>.
- [116] Oku, T. Direct structure analysis of advanced nanomaterials by high-resolution electron microscopy. *Nanotechnology Reviews*, Vol. 1, No. 5, 2012, pp. 389–425.
- [117] Oku, T. High-resolution electron microscopy and electron diffraction of perovskite-type superconducting copper oxides. *Nanotechnology Reviews*, Vol. 3, No. 5, 2014, pp. 413–444.
- [118] Baikie, T., Y. Fang, J. M. Kadro, M. Schreyer, F. Wei, S. G. Mhaisalkar, et al. Synthesis and crystal chemistry of the hybrid perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ for solid-state sensitised solar cell applications. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 1, No. 18, 2013, pp. 5628–5641.
- [119] Chang, J., H. Zhu, J. Xiao, F. H. Isikgor, Z. Lin, Y. Hao, et al. Enhancing the planar heterojunction perovskite solar cell performance through tuning the precursor ratio. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 4, No. 20, 2016, pp. 7943–7949.
- [120] Saliba, M., J. P. Correa-Baena, C. M. Wolff, M. Stollerfoht, N. Phung, S. Albrecht, et al. How to make over 20% efficient perovskite solar cells in regular ($n-i-p$) and inverted ($p-i-n$) architectures. *Chemistry of Materials*, Vol. 30, No. 13, 2018, pp. 4193–4201.
- [121] Zushi, M., A. Suzuki, T. Akiyama, and T. Oku. Fabrication and Characterization of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ -based Photovoltaic Devices. *Chemistry Letters*, Vol. 43, No. 6, 2014, pp. 916–918.
- [122] Oku, T., N. Kakuta, K. Kobayashi, A. Suzuki, and K. Kikuchi. Fabrication and characterization of TiO_2 -based dye-sensitized solar cells. *Progress in Natural Science: Materials International*, Vol. 21, No. 2, 2011, pp. 122–126.
- [123] Oku, T., M. Zushi, Y. Imanishi, A. Suzuki, and K. Suzuki. Microstructures and photovoltaic properties of perovskite-type $\text{CH}_3\text{NH}_3\text{PbI}_3$ compounds. *Applied Physics Express*, Vol. 7, No. 12, 2014, 121601-1–4.
- [124] Oku, T., A. Takeda, A. Nagata, H. Kidowaki, K. Kumada, K. Fujimoto, et al. Microstructures and photovoltaic properties of C_{60} based solar cells with copper oxides, CuInS_2 , phthalocyanines, porphyrin, PVK, nanodiamond, germanium and exciton diffusion blocking layers. *Materials Technology*, Vol. 28, No. 1-2, 2013, pp. 21–39.
- [125] Oku, T., H. Wakimoto, A. Otsuki, and M. Murakami. NiGe-based ohmic contacts to n -type GaAs. I. Effects of In addition. *Journal of Applied Physics*, Vol. 75, No. 5, 1994, pp. 2522–2529.
- [126] Ueoka, N., and T. Oku. Stability characterization of PbI_2 -added $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ photovoltaic devices. *ACS Applied Materials & Interfaces*, Vol. 10, No. 51, 2018, pp. 44443–44451.
- [127] Wang, L., C. McCleese, A. Kovalsky, Y. Zhao, and C. Burda. Femtosecond time-resolved transient absorption spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films: Evidence for passivation effect of PbI_2 . *Journal of the American Chemical Society*, Vol. 136, No. 35, 2014, pp. 12205–12208.
- [128] Chen, Q., H. Zhou, T. B. Song, S. Luo, Z. Hong, H. S. Duan, et al. Controllable self-induced passivation of hybrid lead iodide

- perovskites toward high performance solar cells. *Nano Letters*, Vol. 14, No. 7, 2014, pp. 4158–4163.
- [129] Roldán-Carmona, C., P. Gratiá, I. Zimmermann, G. Grancini, P. Gao, M. Graetzel, and M. K. Nazeeruddin. High efficiency methylammonium lead triiodide perovskite solar cells: The relevance of non-stoichiometric precursors. *Energy & Environmental Science*, Vol. 8, No. 12, 2015, pp. 3550–3556.
- [130] Guo, Y., K. Shoyama, W. Sato, Y. Matsuo, K. Inoue, K. Harano, et al. Chemical pathways connecting lead(II) iodide and perovskite via polymeric plumbate(II) fiber. *Journal of the American Chemical Society*, Vol. 137, No. 50, 2015, pp. 15907–15914.
- [131] Zhang, T., N. Guo, G. Qian, X. Li, and Y. Zhao. A controllable fabrication of grain boundary PbI_2 nanoplates passivated lead halide perovskites for high performance solar cells. *Nano Energy*, Vol. 26, 2016, pp. 50–56.
- [132] Ueoka, N., T. Oku, H. Tanaka, A. Suzuki, H. Sakamoto, M. Yamada, et al. Effects of PbI_2 addition and TiO_2 electron transport layers for perovskite solar cells. *Japanese Journal of Applied Physics*, Vol. 57, No. 7, 2018, 08RE05-1–7.
- [133] Ueoka, N., T. Oku, and A. Suzuki. Effects of excess PbI_2 addition to $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite solar cells. *Chemistry Letters*, Vol. 47, No. 4, 2018, pp. 528–531.
- [134] Mashiyama, H., Y. Kurihara, and T. Azetsu. Disordered cubic perovskite structure of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$). *Journal of the Korean Physical Society*, Vol. 32, 1998, pp. S156–S158.
- [135] Chen, T., B. J. Foley, B. Ipek, M. Tyagi, J. R. P. Copley, C. M. Brown, et al. Rotational dynamics of organic cations in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. *Physical Chemistry Chemical Physics*, Vol. 17, No. 46, 2015, pp. 31278–31286.
- [136] Whitfield, P. S., N. Herron, W. E. Guise, K. Page, Y. Q. Cheng, I. Milas, and M. K. Crawford. Structures, phase transitions and tricritical behavior of the hybrid perovskite methyl ammonium lead iodide. *Scientific Reports*, Vol. 6, 2016, 35685-1-15.
- [137] Saliba, M., and J. P. Correa-Baena. M. Grätzel, A. Hagfeldt, and A. Abate. Perovskite solar cells: from the atomic level to film quality and device performance. *Angewandte Chemie International Edition*, Vol. 57, 2018, pp. 2554–2569.
- [138] Saliba, M., M. Stollerfoht, C. M. Wolff, D. Neher, and A. Abate. Measuring aging stability of perovskite solar cells. *Joule*, Vol. 2, No. 6, 2018, pp. 1019–1024.
- [139] Saliba, M. Perovskite solar cells must come of age. *Science*, Vol. 359, No. 6374, 2018, pp. 388–389.
- [140] Zhou, Y. and Y. Zhao. Chemical stability and instability of inorganic halide perovskites. *Energy & Environmental Science*, Vol. 12, No. 5, 2019, pp. 1495–1511.
- [141] Travis, W., E. N. K. Glover, H. Bronstein, D. O. Scanlon, and R. G. Palgrave. On the application of the tolerance factor to inorganic and hybrid halide perovskites: A revised system. *Chemical Science (Cambridge)*, Vol. 7, No. 7, 2016, pp. 4548–4556.
- [142] Hoefler, S. F., G. Trimmel, and T. Rath. Progress on lead-free metal halide perovskites for photovoltaic applications: A review. *Monatshefte für Chemie*, Vol. 148, No. 5, 2017, pp. 795–826.
- [143] Li, Z., M. Yang, J. S. Park, S. H. Wei, J. J. Berry, and K. Zhu. Perovskite structures by tuning tolerance factor: Formation of formamidinium and cesium lead iodide solid-state alloys. *Chemistry of Materials*, Vol. 28, No. 1, 2016, pp. 284–292.
- [144] Tanaka, H., T. Oku, and N. Ueoka. Structural stabilities of organic-inorganic perovskite crystals. *Japanese Journal of Applied Physics*, Vol. 57, 2018, 08RE12-1–9.
- [145] Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica. Section A, Crystal Physics, Diffraction, Theoretical and General Crystallography*, Vol. 32, No. 5, 1976, pp. 751–767.
- [146] Li, C., X. Lu, W. Ding, L. Feng, Y. Gao, and Z. Guo. Formability of ABX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) halide perovskites. *Acta Crystallographica. Section B, Structural Science*, Vol. 64, No. Pt 6, 2008, pp. 702–707.
- [147] Kieslich, G., S. Sun, and A. K. Cheetham. An extended Tolerance Factor approach for organic–inorganic perovskites. *Chemical Science (Cambridge)*, Vol. 6, No. 6, 2015, pp. 3430–3433.
- [148] Sampson, M. D., J. S. Park, R. D. Schaller, M. K. Y. Chan, and A. B. F. Martinson. Transition metal-substituted lead halide perovskite absorbers. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 5, No. 7, 2017, pp. 3578–3588.
- [149] Xiao, Z. and Y. Yan, Progress in theoretical study of metal halide perovskite solar cell materials. *Advanced Energy Materials*, Vol. 7, 2017, 1701136-1-20.
- [150] Bartel, C. J., C. Sutton, B. R. Goldsmith, R. Ouyang, C. B. Musgrave, L. M. Ghiringhelli, and M. Scheffler. New tolerance factor to predict the stability of perovskite oxides and halides. *Science Advances*, Vol. 5, No. 2, 2019, eaav0693-1–9.
- [151] Körbel, S., M. A. L. Marques, and S. Botti. Stability and electronic properties of new inorganic perovskites from high-throughput ab initio calculations. *Journal of Materials Chemistry. C, Materials for Optical and Electronic Devices*, Vol. 4, No. 15, 2016, pp. 3157–3167.
- [152] Suzuki, A., and T. Oku. First-principles calculation study of electronic structures and magnetic properties of Mn-doped perovskite crystals for solar cell applications. *Japanese Journal of Applied Physics*, Vol. 57, 2018, 02CE04-1–7.
- [153] Suzuki, A., and T. Oku. Effects of transition metals incorporated into perovskite crystals on the electronic structures and magnetic properties by first-principles calculation. *Heliyon*, Vol. 4, No. 8, 2018, e00755-1–22.
- [154] Suzuki, A., and T. Oku. First-principles calculation study of electronic structures of alkali metals (Li, K, Na and Rb)-incorporated formamidinium lead halide perovskite compounds. *Applied Surface Science*, Vol. 483, 2019, pp. 912–921.
- [155] Weber, D. Z. $\text{CH}_3\text{NH}_3\text{PbX}_3$, ein Pb(II)-system mit kubischer perowskitstruktur / $\text{CH}_3\text{NH}_3\text{PbX}_3$, a Pb(II)-system with cubic perovskite structure. *Zeitschrift für Naturforschung B*, Vol. 33, No. 12, 1978, pp. 1443–1445. (in German)
- [156] Poglitsch, A. and D. Weber. Dynamic disorder in methylammoniumtrihalogenoplumbates (II) observed by millimeter-wave spectroscopy. *Journal of Chemical Physics*, Vol. 87, No. 11, 1987, pp. 6373–6378.
- [157] Onoda-Yamamuro, N., T. Matsuo, and H. Suga. Calorimetric and IR spectroscopic studies of phase transitions in methylammonium trihalogenoplumbates (II). *Journal of Physics and Chemistry of Solids*, Vol. 51, No. 12, 1990, pp. 1383–1395.
- [158] Kawamura, Y., H. Mashiyama, and K. Hasebe. Structural study on cubic–tetragonal transition of $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Journal of the Physical Society of Japan*, Vol. 71, No. 7, 2002, pp. 1694–1697.
- [159] Ren, Y., I. W. H. Oswald, X. Wang, G. T. McCandless, and J. Y. Chan. Orientation of organic cations in hybrid inorganic-organic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ from subatomic resolution single crystal neutron diffraction structural studies. *Crystal Growth & Design*, Vol. 16, No. 5, 2016, pp. 2945–2951.

- [160] Weller, M. T., O. J. Weber, P. F. Henry, A. M. Di Pumpo, and T. C. Hansen. Complete structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K. *Chemical Communications (Cambridge)*, Vol. 51, No. 20, 2015, pp. 4180–4183.
- [161] Stoumpos, C. C., C. D. Malliakas, and M. G. Kanatzidis. Semi-conducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorganic Chemistry*, Vol. 52, No. 15, 2013, pp. 9019–9038.
- [162] Momma, K., and F. Izumi. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, Vol. 44, No. 6, 2011, pp. 1272–1276.
- [163] Motta, C., F. El-Mellouhi, S. Kais, N. Tabet, F. Alharbi, and S. Sanvito. Revealing the role of organic cations in hybrid halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Nature Communications*, Vol. 6, 2015, 7026-1-7.
- [164] Brivio, F., J. M. Frost, J. M. Skelton, A. J. Jackson, O. J. Weber, M. T. Weller, et al. Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide. *Physical Review B: Condensed Matter and Materials Physics*, Vol. 91, 2015, 144308-1–8.
- [165] Zhou, Y., A. L. Vasiliev, W. Wu, M. Yang, S. Pang, K. Zhu, and N. P. Padture. Crystal morphologies of organolead trihalide in mesoscopic/planar perovskite solar cells. *Journal of Physical Chemistry Letters*, Vol. 6, No. 12, 2015, pp. 2292–2297.
- [166] Zhou, Y., H. Sternlicht, and N. P. Padture. Transmission electron microscopy of halide perovskite materials and devices. *Joule*, Vol. 3, No. 3, 2019, pp. 641–661.
- [167] Weller, M. T., O. J. Weber, J. M. Frost, and A. Walsh. Cubic perovskite structure of black formamidinium lead iodide, α - $[\text{HC}(\text{NH}_2)_2]\text{PbI}_3$, at 298 K. *Journal of Physical Chemistry Letters*, Vol. 6, No. 16, 2015, pp. 3209–3212.
- [168] Zhou, Y., Z. Zhou, M. Chen, Y. Zong, J. Huang, S. Pang, and N. P. Padture. Doping and alloying for improved perovskite solar cells. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 4, No. 45, 2016, pp. 17623–17635.
- [169] Mashiyama, H., Y. Kawamura, E. Magome, and Y. Kubota. Displacive character of the cubic-tetragonal transition in $\text{CH}_3\text{NH}_3\text{PbX}_3$. *Journal of the Korean Physical Society*, Vol. 42, 2003, pp. S1026–S1029.
- [170] Yamada, K., K. Mikawa, T. Okuda, and K. S. Knight. Static and dynamic structures of $\text{CD}_3\text{ND}_3\text{GeCl}_3$ studied by TOF high resolution neutron powder diffraction and solid state NMR. *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry*, No. 10, 2002, pp. 2112–2118.
- [171] Yamada, K., Y. Kuranaga, K. Ueda, S. Goto, T. Okuda, and Y. Furukawa. Phase transition and electric conductivity of AsSnCl_3 ($\text{A} = \text{Cs}$ and CH_3NH_3). *Bulletin of the Chemical Society of Japan*, Vol. 71, No. 1, 1998, pp. 127–134.
- [172] Schueller, E. C., G. Laurita, D. H. Fabini, C. C. Stoumpos, M. G. Kanatzidis, and R. Seshadri. Crystal structure evolution and notable thermal expansion in hybrid perovskites formamidinium tin iodide and formamidinium lead bromide. *Inorganic Chemistry*, Vol. 57, No. 2, 2018, pp. 695–701.
- [173] Sutton, R. J., M. R. Filip, A. A. Haghighirad, N. Sakai, B. Wenger, F. Giustino, and H. J. Snaith. Cubic or orthorhombic? Revealing the crystal structure of metastable black-phase CsPbI_3 by theory and experiment. *ACS Energy Letters*, Vol. 3, No. 8, 2018, pp. 1787–1794.
- [174] Rodová, M., J. Brožek, K. Knížek, and K. Nitsch. Phase transitions in ternary caesium lead bromide. *Journal of Thermal Analysis and Calorimetry*, Vol. 71, No. 2, 2003, pp. 667–673.
- [175] Chung, I., J. H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, et al. CsSnI_3 : Semiconductor or metal? High electrical conductivity and strong near-infrared photoluminescence from a single material. High hole mobility and phase-transitions. *Journal of the American Chemical Society*, Vol. 134, No. 20, 2012, pp. 8579–8587.
- [176] Scaife, D. E., P. F. Weller, and W. G. Fisher. Crystal preparation and properties of cesium tin(II) trihalides. *Journal of Solid State Chemistry*, Vol. 9, No. 3, 1974, pp. 308–314.
- [177] Thiele, G., H. W. Rotter, and K. D. Schmidt. Kristallstrukturen und phasentransformationen von caesiumtrihalogenogermanaten(II) CsGeX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 545, No. 2, 1987, pp. 148–156. (in German)
- [178] Thiele, G., H. W. Rotter, and K. D. Schmidt. Die Kristallstrukturen und phasentransformationen des tetramorphen RbGeI_3 . *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 571, No. 1, 1989, pp. 60–68. (in German)
- [179] Thiele, G., H. W. Rotter, and K. D. Schmidt. Die Kristallstrukturen und phasentransformationen von RbGeBr_3 . *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 559, No. 1, 1988, pp. 7–16. (in German)
- [180] Pan, Z., H. Rao, I. Mora-Seró, J. Bisquert, and X. Zhong. Quantum dot-sensitized solar cells. *Chemical Society Reviews*, Vol. 47, No. 20, 2018, pp. 7659–7702.
- [181] Galar, P., P. Piatkowski, T. T. Ngo, M. Gutiérrez, I. Mora-Seró, and A. Douhal. Perovskite-quantum dots interface: Deciphering its ultrafast charge carrier dynamics. *Nano Energy*, Vol. 49, 2018, pp. 471–480.
- [182] Slavney, A. H., T. Hu, A. M. Lindenberg, and H. I. Karunadasa. A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. *Journal of the American Chemical Society*, Vol. 138, No. 7, 2016, pp. 2138–2141.
- [183] McClure, E. T., M. R. Ball, W. Windl, and P. M. Woodward. $\text{Cs}_2\text{AgBiX}_6$ ($\text{X} = \text{Br}, \text{Cl}$): New visible light absorbing, lead-free halide perovskite semiconductors. *Chemistry of Materials*, Vol. 28, No. 5, 2016, pp. 1348–1354.
- [184] Zhou, J., Z. Xia, M. S. Molokeev, X. Zhang, D. Peng, and Q. Liu. Composition design, optical gap and stability investigations of lead-free halide double perovskite $\text{Cs}_2\text{AgInCl}_6$. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 5, No. 29, 2017, pp. 15031–15037.
- [185] Majher, J. D., M. B. Gray, T. A. Strom, and P. M. Woodward. $\text{Cs}_2\text{NaBiCl}_6:\text{Mn}^{2+}$ —A new orange-red halide double perovskite phosphor. *Chemistry of Materials*, Vol. 31, No. 5, 2019, pp. 1738–1744.
- [186] Wei, F., Z. Deng, S. Sun, F. Zhang, D. M. Evans, G. Kieslich, et al. Synthesis and properties of a lead-free hybrid double perovskite: $(\text{CH}_3\text{NH}_3)_2\text{AgBiBr}_6$. *Chemistry of Materials*, Vol. 29, 2017, pp. 1089–1094.
- [187] Wei, F., Z. Deng, S. Sun, F. Xie, G. Kieslich, D. M. Evans, et al. The synthesis, structure and electronic properties of a lead-free hybrid inorganic–organic double perovskite $(\text{MA})_2\text{KBiCl}_6$ ($\text{MA} = \text{methylammonium}$). *Materials Horizons*, Vol. 3, No. 4, 2016, pp. 328–332.
- [188] Sabry-Grant, R., M. Vickers, and J. K. Cockcroft. A detailed study of the variation in lattice parameter and structure with temperature and dilution in yttrium-substituted holmium hexachloro-

- elposolite $\text{Cs}_2\text{NaY}_x\text{Ho}_{1-x}\text{Cl}_6$. *Zeitschrift für Kristallographie*, Vol. 222, No. 7, 2007, pp. 356–364.
- [189] Acevedo, R. and V. Poblete. Synthesis and X-ray powder diffraction study of the elposolite $\text{Cs}_2\text{NaCeCl}_6$. *Powder Diffraction*, Vol. 10, No. 4, 1995, pp. 241–242.
- [190] Poblete, V., R. Acevedo, and P. A. Tanner, Spectroscopic studies, theoretical models and structural characterization. I. The elposolites $\text{Cs}_2\text{NaLnCl}_6$, where $\text{Ln}^{3+} = \text{Er}^{3+}, \text{Yb}^{3+}$, II. Synthesis and X-ray powder diffraction of the elposolites $\text{Cs}_2\text{NaSmCl}_6$. *Revista Mexicana de Física*, Vol. 44S1, 1998, pp. 29–32.
- [191] Reber, C., H. U. Guedel, G. Meyer, T. Schleid, and C. A. Daul. Optical spectroscopic and structural properties of V^{3+} -doped fluoride, chloride, and bromide elposolite lattices. *Inorganic Chemistry*, Vol. 28, No. 16, 1989, pp. 3249–3258.
- [192] Meyer, G., S. J. Hwu, and J. D. Corbett. Low-temperature crystal growth of $\text{Cs}_2\text{LiLuCl}_6$ -II and $\text{Cs}_2\text{KScCl}_6$ under reducing conditions and their structural refinement. *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 535, No. 4, 1986, pp. 208–212.
- [193] Barbier, P., M. Drache, G. Mairesse, and J. Ravez. Phase transitions in a $\text{Cs}_{2-x}\text{K}_{1+x}\text{BiCl}_6$ solid solution. *Journal of Solid State Chemistry*, Vol. 42, No. 2, 1982, pp. 130–135.
- [194] Friedrich, G., H. Fink, and H. J. Seifert. Über alkalihexachlorochromate(III): Na_3CrCl_6 . *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 548, No. 5, 1987, pp. 141–150.
- [195] Villafuerte-Castrejón, M. E., M. R. E. Yáñez, J. Gómez-Lara, and R. Pomés. Crystal structure of $\text{Cs}_2\text{KTbCl}_6$ and $\text{Cs}_2\text{KEuCl}_6$ by powder X-ray diffraction. *Journal of Solid State Chemistry*, Vol. 132, No. 1, 1997, pp. 1–5.
- [196] P. Gaille, and J. C. Cousseins. Chimie minérale. Nouvelles pérovskites chlorées du type $\text{Cs}_2\text{KB}_3\text{Cl}_6$. *Comptes Rendus des Seances de l'Academie des Sciences, Serie C: Sciences Chimiques*, Vol. 272, 1971, pp. 1328–1330.
- [197] Bohnsack, A., and G. Meyer. Crystal structure of dirubidium lithium dysprosium(III) hexabromide, $\text{Rb}_2\text{LiDyBr}_6$. *Zeitschrift für Kristallographie. New Crystal Structures*, Vol. 212, No. 1, 1997, p. 2.
- [198] Meyer, G., and E. Dietzel. Zur struktursystematik der elpasolith-familie: Neue chloride $\text{A}_2^+\text{B}^+\text{M}^{3+}\text{Cl}_6$ ($\text{A}^+ = \text{Rb}, \text{Ti}, \text{In}, \text{K}$; $\text{B}^+ = \text{Li}, \text{Ag}, \text{Na}$) *Revue de Chimie Minerale*, Vol. 16, 1979, pp. 189–202.
- [199] Qiu, L., L. K. Ono, and Y. Qi. Advances and challenges to the commercialization of organic–inorganic halide perovskite solar cell technology. *Materials Today Energy*, Vol. 7, 2018, pp. 169–189.
- [200] Giustino, F., and H. J. Snaith. Toward lead-free perovskite solar cells. *ACS Energy Letters*, Vol. 1, No. 6, 2016, pp. 1233–1240.
- [201] Savory, C. N., and A. Walsh. Can Pb-free halide double perovskites support high-efficiency solar cells? *ACS Energy Letters*, Vol. 1, 2016, pp. 949–955.
- [202] Yang, P., F. P. Doty, M. A. Rodriguez, M. R. Sanchez, X. Zhou, and K. S. Shah. The synthesis and structure of elpasolite halide scintillators. *Materials Research Society Symposium Proceedings*, Vol. 1164, 2009, pp. 185–192.
- [203] Gundiah, G., K. Brennan, Z. Yan, E. C. Samulon, G. Wu, G. A. Bizarri, et al. Structure and scintillation properties of Ce^{3+} -activated $\text{Cs}_2\text{NaLaCl}_6$, Cs_3LaCl_6 , $\text{Cs}_2\text{NaLaBr}_6$, Cs_3LaBr_6 , $\text{Cs}_2\text{NaLaI}_6$ and Cs_3LaI_6 . *Journal of Luminescence*, Vol. 149, 2014, pp. 374–384.
- [204] Wei, H., M. H. Du, L. Stand, Z. Zhao, H. Shi, M. Zhuravleva, and C. L. Melcher. Scintillation properties and electronic structures of the intrinsic and extrinsic mixed elpasolites $\text{Cs}_2\text{NaRBr}_3\text{I}_3$ ($\text{R} = \text{La}, \text{Y}$). *Physical Review Applied*, Vol. 5, No. 2, 2016, pp. 024008-1-13.
- [205] Mitzi, D. B. Templating and structural engineering in organic–inorganic perovskites. *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry*, No. 1, 2001, pp. 1–12.
- [206] Xiao, Z., W. Meng, J. Wang, D. B. Mitzi, and Y. Yan. Searching for promising new perovskite-based photovoltaic absorbers: The importance of electronic dimensionality. *Materials Horizons*, Vol. 4, No. 2, 2017, pp. 206–216.
- [207] Tang, G., Z. Xiao, H. Hosono, T. Kamiya, D. Fang, and J. Hong. Layered halide double perovskites $\text{Cs}_{3+n}\text{M(II)}_n\text{Sb}_2\text{X}_{9+3n}$ ($\text{M} = \text{Sn}, \text{Ge}$) for photovoltaic applications. *Journal of Physical Chemistry Letters*, Vol. 9, No. 1, 2018, pp. 43–48.
- [208] Mao, L., W. Ke, L. Pedesseau, Y. Wu, C. Katan, J. Even, et al. Hybrid Dion-Jacobson 2D lead iodide perovskites. *Journal of the American Chemical Society*, Vol. 140, No. 10, 2018, pp. 3775–3783.
- [209] Stoumpos, C. C., D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, and M. G. Kanatzidis. Ruddlesden–Popper hybrid lead iodide perovskite 2D homologous semiconductors. *Chemistry of Materials*, Vol. 28, No. 8, 2016, pp. 2852–2867.
- [210] Cortecchia, D., H. A. Dewi, J. Yin, A. Bruno, S. Chen, T. Baikie, et al. Lead-free $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ hybrid perovskites. *Inorganic Chemistry*, Vol. 55, No. 3, 2016, pp. 1044–1052.
- [211] Kassou, S., A. Kaiba, P. Guionneau, and A. Belaaraj. Organic–inorganic hybrid perovskite $(\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3)_2\text{CdCl}_4$: Synthesis, structural and thermal properties. *Journal of Structural Chemistry*, Vol. 57, No. 4, 2016, pp. 737–743.
- [212] Mao, L., S. M. L. Teicher, C. C. Stoumpos, R. M. Kennard, R. A. DeCrescent, G. Wu, et al. Chemical and structural diversity of hybrid layered double perovskite halides. *Journal of the American Chemical Society*, Vol. 141, No. 48, 2019, pp. 19099–19109.
- [213] Kihara, K., and T. Sudo. The structure of α -type cesium antimony nonachloride, $\text{Cs}_3\text{Sb}_2\text{Cl}_9$. *Zeitschrift für Kristallographie*, Vol. 134, 1971, pp. 142–144.
- [214] Kihara, K., and T. Sudo. The crystal structures of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$. *Acta Crystallographica. Section B, Structural Crystallography and Crystal Chemistry*, Vol. 30, No. 4, 1974, pp. 1088–1093.
- [215] Jongen, L., T. Gloger, J. Beekhuizen, and G. Meyer. Divalent titanium: The halides ATiX_3 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$). *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 631, No. 2-3, 2005, pp. 582–586.
- [216] Meyer, G., D. J. Hinz, and U. Floerke. Crystal structure of caesium titanium tribromide, CsTiBr_3 . *Zeitschrift für Kristallographie*, Vol. 208, 1993, pp. 370–371.
- [217] Zhang, J., and J. D. Corbett. Synthesis and structure of the novel layered phase CsTi_2Cl_7 . *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 58, No. 1, 1990, pp. 36–44.
- [218] Zhu, X. H., N. Mercier, M. Allain, P. Frère, P. Blanchard, J. Roncali, and A. Riou. Crystal structure of $(\text{NH}_3-\text{R}-\text{NH}_3)(\text{NH}_3-\text{R}-\text{NH}_2)\text{PbI}_5$ ($\text{R} = 5,5'$ -bis(ethylsulfanyl)-2,2'-bithiophene): $\text{NH}_3 \cdots \text{NH}_2$ interaction as a tool to reach densely packed organic layers in organic–inorganic perovskites. *Journal of Solid State Chemistry*, Vol. 177, No. 4-5, 2004, pp. 1067–1071.
- [219] Zhou, J., J. Luo, X. Rong, P. Wei, M. S. Molokeev, Y. Huang, et al. Lead-free perovskite derivative $\text{Cs}_2\text{SnCl}_{6-x}\text{Br}_x$ single crystals for narrowband photodetectors. *Advanced Optical Materials*, Vol. 7, No. 10, 2019, p. 1900139.
- [220] Brill, T. B., R. C. Gearhart, and W. A. Welsh. Crystal structures of M_2SnCl_6 salts. An analysis of the “crystal field effect” in their

- nuclear quadrupole resonance and vibrational spectra. *Journal of Magnetic Resonance (San Diego, Calif.)*, Vol. 13, 1974, pp. 27–37.
- [221] Velázquez, M., A. Ferrier, S. Péchev, P. Gravereau, J. P. Chaminade, X. Portier, and R. Moncorgé. Growth and characterization of pure and Pr^{3+} -doped Cs_4PbBr_6 crystals. *Journal of Crystal Growth*, Vol. 310, No. 24, 2008, pp. 5458–5463.
- [222] Cenxual, K., L. M. Gelato, M. Penzo, and E. Parté. Overlooked trigonal symmetry in structures reported with monoclinic centred Bravais lattices; trigonal description of Li_8Pb_3 , PtTe , Pt_3Te_4 , Pt_2Te_3 , LiFe_6Ge_4 , LiFe_6Ge_5 , $\text{CaGa}_6\text{Te}_{10}$ and $\text{La}_{3.266}\text{Mn}_{1.1}\text{S}_6$. *Zeitschrift für Kristallographie*, Vol. 193, 1990, pp. 217–242.
- [223] Sinram, D., C. J. Brendal, and B. Krebs. Hexa-iodoanions of titanium, zirconium, hafnium, palladium and platinum: Preparation, properties and crystal structures of the caesium salts. *Inorganica Chimica Acta*, Vol. 64, 1982, pp. L131–L132.
- [224] Wendling, E., and J. De Lavillandre. Caractérisation d'espèces chloroperoxytitaniques en solution aqueuse chlorhydrique, perchlorique et en solution dans l'acide formique. Chloroperoxytitanates du type $\text{M}_2(\text{TiO}_2\text{Cl}_4, \text{H}_2\text{O})$ ($\text{M} = \text{Rb}, \text{Cs}$) *Bulletin de la Société Chimique de France*, Vol. 2, 1967, pp. 2142–2148.
- [225] Maughan, A. E., A. M. Ganose, M. M. Bordelon, E. M. Miller, D. O. Scanlon, and J. R. Neilson. Defect tolerance to intolerance in the vacancy-ordered double perovskite semiconductors Cs_2SnI_6 and Cs_2TeI_6 . *Journal of the American Chemical Society*, Vol. 138, No. 27, 2016, pp. 8453–8464.
- [226] Maughan, A. E., A. M. Ganose, M. A. Almaker, D. O. Scanlon, and J. R. Neilson. Tolerance factor and cooperative tilting effects in vacancy-ordered double perovskite halides. *Chemistry of Materials*, Vol. 30, No. 11, 2018, pp. 3909–3919.
- [227] Abriel, W. and E. J. Zehnder. Vibronic coupling and dynamically distorted structures in hexahalogenotellurates(IV): low temperature X-ray diffraction (300–160 K) and FTIR-spectroscopic (300–5 K) Results [1]. *Zeitschrift für Naturforschung*, Vol. 42b, 1987, pp. 1273–1281.
- [228] Thiele, G., C. Mrozek, and K. Wittmann. On Hexaiodoplatinates(IV) M_2PtI_6 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Ti}$) – Preparation, properties and structural data. *Zeitschrift für Naturforschung*, Vol. 38, 1983, pp. 905–910.
- [229] Restori, R., and D. Schwarzenbach. Anharmonic motion vs chemical bonding: On the interpretation of electron densities determined by X-ray diffraction. *Acta Crystallographica. Section A, Foundations of Crystallography*, Vol. 52, No. 3, 1996, pp. 369–378.
- [230] Yamada, K., H. Sera, S. Sawada, H. Tada, T. Okada, and H. Tanaka. Reconstructive phase transformation and kinetics of $\text{Cs}_3\text{Sb}_2\text{I}_9$ by means of Rietveld analysis of X-Ray diffraction and ^{127}I NQR. *Journal of Solid State Chemistry*, Vol. 134, No. 2, 1997, pp. 319–325.
- [231] Arakcheeva, A. V., G. Chapuis, and M. Meyer. The LT phase of $\text{Cs}_3\text{Bi}_2\text{I}_9$. *Zeitschrift für Kristallographie*, Vol. 216, 2001, pp. 199–205.
- [232] Xu, F., T. Zhang, G. Li, and Y. Zhao. Mixed cation hybrid lead halide perovskites with enhanced performance and stability. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, Vol. 5, No. 23, 2017, pp. 11450–11461.
- [233] Rodríguez-Romero, J., B. C. Hames, I. Mora-Seró, and E. M. Barea. Conjugated organic cations to improve the optoelectronic properties of 2D/3D perovskites. *ACS Energy Letters*, Vol. 2, No. 9, 2017, pp. 1969–1970.
- [234] Rodríguez-Romero, J., B. Clasen Hames, P. Galar, A. Fakharuddin, I. Suarez, L. Schmidt-Mende, et al. Tuning optical/electrical properties of 2D/3D perovskite by the inclusion of aromatic cation. *Physical Chemistry Chemical Physics*, Vol. 20, No. 48, 2018, pp. 30189–30199.
- [235] Fan, J., Y. Ma, C. Zhang, C. Liu, W. Li, R.E.I. Schropp, and Y. Mai. Thermodynamically self-healing 1D-3D hybrid perovskite solar cells. *Advanced Energy Materials*, Vol. 8, 2018, 1703421-1-8.
- [236] Gong, J., M. Flatken, A. Abate, J. P. Correa-Baena, I. Mora-Seró, M. Saliba, and Y. Zhou. The bloom of perovskite optoelectronics: Fundamental science matters. *ACS Energy Letters*, Vol. 4, No. 4, 2019, pp. 861–865.
- [237] Lee, B., C. C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C. Y. Yeh, et al. Air-stable molecular semiconducting iodosalts for solar cell applications: Cs_2SnI_6 as a hole conductor. *Journal of the American Chemical Society*, Vol. 136, No. 43, 2014, pp. 15379–15385.
- [238] Maughan, A. E., A. M. Ganose, D. O. Scanlon, and J. R. Neilson. Perspectives and design principles of vacancy-ordered double perovskite halide semiconductors. *Chemistry of Materials*, Vol. 31, No. 4, 2019, pp. 1184–1195.
- [239] Dai, W. B., S. Xu, J. Zhou, J. Hu, K. Huang, and M. Xu. Lead-free, stable, and effective double $\text{FA}_4\text{Ge}^{\text{II}}\text{Sb}^{\text{III}}\text{Cl}_{12}$ perovskite for photovoltaic applications. *Solar Energy Materials and Solar Cells*, Vol. 192, 2019, pp. 140–146.
- [240] Ju, M. G., M. Chen, Y. Zhou, H. F. Garces, J. Dai, L. Ma, et al. Earth-abundant nontoxic titanium(IV)-based vacancy-ordered double perovskite halides with tunable 1.0 to 1.8 eV bandgaps for photovoltaic applications. *ACS Energy Letters*, Vol. 3, No. 2, 2018, pp. 297–304.
- [241] Willett, R., H. Place, and M. Middleton. Crystal structures of three new copper(II) halide layered perovskites: Structural, crystallographic, and magnetic correlations. *Journal of the American Chemical Society*, Vol. 110, No. 26, 1988, pp. 8639–8650.
- [242] Pabst, I., H. Fuess, and J. W. Bats. Structure of monomethylammonium tetrachlorocuprate at 297 and 100 K. *Acta Crystallographica. Section C, Crystal Structure Communications*, Vol. 43, No. 3, 1987, pp. 413–416.
- [243] Zuo C., and L. Ding. An 80.11% FF record achieved for perovskite solar cells by using the NH_4Cl additive. *Nanoscale*, Vol. 6, No. 17, 2014, pp. 9935–9938.
- [244] Zhou, Y., O. S. Game, S. Pang, and N. P. Padture. Microstructures of organometal trihalide perovskites for solar cells: Their evolution from solutions and characterization. *Journal of Physical Chemistry Letters*, Vol. 6, No. 23, 2015, pp. 4827–4839.
- [245] Zhou, Y., M. Yang, W. Wu, A. L. Vasiliev, K. Zhu, and N. P. Padture. Room-temperature crystallization of hybrid-perovskite thin films via solvent–solvent extraction for high-performance solar cells. *Journal of Materials Chemistry A*, Vol. 3, No. 15, 2015, pp. 8178–8184.
- [246] Oku, T., Y. Ohishi, and N. Ueoka. Highly (100)-oriented $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Cl) perovskite solar cells prepared with NH_4Cl using an air blow method. *RSC Advances*, Vol. 8, No. 19, 2018, pp. 10389–10395.
- [247] Oku, T., Y. Ohishi, A. Suzuki, and Y. Miyazawa. Effects of NH_4Cl addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices. *Journal of the Ceramic Society of Japan*, Vol. 125, No. 4, 2017, pp. 303–307.
- [248] Yu, H., F. Wang, F. Xie, W. Li, J. Chen, and N. Zhao. The role of chlorine in the formation process of “ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ” perovskite.

- Advanced Functional Materials*, Vol. 24, 2014, pp. 7102–7108.
- [249] Dualeh, A., N. Ttreault, T. Moehl, P. Gao, M. K. Nazeeruddin, and M. Grtzel. Effect of annealing temperature on film morphology of organic-inorganic hybrid perovskite solid-state solar cells. *Advanced Functional Materials*, Vol. 24, No. 21, 2014, pp. 3250–3258.
- [250] McLeod, J. A., Z. Wu, B. Sun, and L. Liu. The influence of the I/Cl ratio on the performance of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ -based solar cells: why is $\text{CH}_3\text{NH}_3\text{I} : \text{PbCl}_2 = 3 : 1$ the “magic” ratio? *Nanoscale*, Vol. 8, No. 12, 2016, pp. 6361–6368.
- [251] Oku, T., and Y. Ohishi. Effects of annealing on $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ perovskite photovoltaic devices. *Journal of the Ceramic Society of Japan*, Vol. 126, No. 1, 2018, pp. 56–60.
- [252] Umemoto, Y., A. Suzuki, and T. Oku. Effects of halogen doping on the photovoltaic properties of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ perovskite solar cells. *AIP Conference Proceedings*, Vol. 1807, 2017, 020011–1–10.
- [253] Oku, T., J. Yamanouchi, Y. Umemoto, and A. Suzuki. Dendritic structures of photovoltaic perovskite crystals. *Materia Japan*, Vol. 57, 2018, p. 601.
- [254] Ivanov, I. L., A. S. Steparuk, M. S. Bolyachkina, D. S. Tsvetkov, A. P. Safronov, and A. Y. Zuev. Thermodynamics of formation of hybrid perovskite-type methylammonium lead halides. *Journal of Chemical Thermodynamics*, Vol. 116, 2018, pp. 253–258.
- [255] Ju, D., Y. Dang, Z. Zhu, H. Liu, C. C. Chueh, X. Li, et al. Tunable band gap and long carrier recombination lifetime of stable mixed $\text{CH}_3\text{NH}_3\text{Pb}_x\text{Sn}_{1-x}\text{Br}_3$ single crystals. *Chemistry of Materials*, Vol. 30, No. 5, 2018, pp. 1556–1565.
- [256] Rietveld, M. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, Vol. 2, No. 2, 1969, pp. 65–71.
- [257] Fu, K., S. S. Lim, Y. Fang, P. P. Boix, N. Mathews, T. C. Sum, et al. Modulating $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite crystallization behavior through precursor concentration. *Nano*, Vol. 9, 2014, pp. 1440003-1-9.
- [258] Ando, Y., T. Oku, and Y. Ohishi. Rietveld refinement of crystal structure of perovskite $\text{CH}_3\text{NH}_3\text{Pb}(\text{Sb})\text{I}_3$ solar cells. *Japanese Journal of Applied Physics*, Vol. 57, No. 2, 2018, 02CE02-1–5.
- [259] Wang, R., J. Wang, S. Tan, Y. Duan, Z. K. Wang, and Y. Yang. Opportunities and challenges of lead-free perovskite optoelectronic devices. *Trends in Chemistry*, Vol. 1, No. 4, 2019, pp. 368–379.
- [260] Izumi, F., and T. Ikeda. A Rietveld-analysis program RIETAN-98 and its applications to zeolites. *Materials Science Forum*, Vol. 198, 2000, pp. 321–324.
- [261] Hames, B. C., R. S. Snchez, A. Fakharuddin, and I. Mora-Ser. A comparative study of light-emitting diodes based on all-inorganic perovskite nanoparticles (CsPbBr_3) synthesized at room temperature and by a hot-injection method. *ChemPlusChem*, Vol. 83, 2018, pp. 294–299.
- [262] Saliba, M., S. M. Wood, J. B. Patel, P. K. Nayak, J. Huang, J. A. Alexander-Webber, et al. Structured organic-inorganic perovskite toward a distributed feedback laser. *Advanced Materials*, Vol. 28, No. 5, 2016, pp. 923–929.
- [263] Xu, X., Y. Zhong, and Z. Shao. Double perovskites in catalysis, electrocatalysis, and photo(electro)catalysis. *Trends in Chemistry*, Vol. 1, No. 4, 2019, pp. 410–424.
- [264] Pan, S., P. Zhang, H. Zhu, J. Zhang, J. Pan, H. Chen, et al. Crystal growth, luminescence and scintillation properties of mixed $\text{Ce}:\text{Cs}_2\text{LiLa}_x\text{Y}_{1-x}\text{Cl}_6$ ($0 < x \leq 0.4$) scintillators. *Journal of Luminescence*, Vol. 201, 2018, pp. 211–216.
- [265] Detection properties and internal activity of newly developed La-containing scintillator crystals. *Nuclear Instruments & Methods in Physics Research, Section A*, Vol. 925, 2019, pp. 70–75.
- [266] Khan, A., P. Q. Vuong, G. Rooh, H. J. Kim, and S. Kim. Crystal growth and Ce^{3+} concentration optimization in Tl_2LaCl_5 : An excellent scintillator for the radiation detection. *Journal of Alloys and Compounds*, Vol. 827, 2020, pp. 154366-1-10.