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# **Doctoral Dissertation**

# Transformation Mechanism of Pb/Sn Perovskites and Exploration of Bi/Sb-Based Semiconductors as an Alternative

(Pb/Snペロブスカイトの変性機構の解明と 代替材料としての Bi/Sb 系半導体の探索)

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January 2021

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## Preface

The studies presented in this dissertation were carried out under the supervision of Prof. Dr. Akinori Saeki at Department of Applied Chemistry, Graduate School of Engineering, Osaka University.

The contents of this dissertation provide the insight into the transformation mechanism of lead and tin halide perovskites with air exposure and the specific thermoresponsive emission behavior, and the fundamental optoelectronic properties and device characteristics of bismuth and antimony-based semiconducting materials for a substitution of halide perovskites. The author hopes these findings will contribute to the development of lead/tin halide perovskites and bismuth/antimony-based semiconductors for optical and optoelectronic applications.

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## **Chapter 1: General Introduction**

The development of renewable energy production system as an alternative to fossil fuels is one of the most important tasks for future human lives. Although a large part of global electricity supply is dependent on fossil fuels, these resources is going on depletion along with the environment destroy. In this viewpoint, the use of solar energy with photovoltaic (PV) cells is expectable. The literature shows the great potential of PV, where calculated annual solar energy potential is 1575-49837 exa Joules, 2.6-82 fold larger than the global energy consumption in 2015.<sup>1,2</sup> With the demand for renewable energy resources, PV technologies are widely developed, and expected to occupy 30% of energy supply in 2100 (Figure 1-1).<sup>1</sup> In fact, conventional crystalline silicon PV achieves power conversion efficiencies more than 20% and 26% in the commercial and lab scale, respectively.<sup>3</sup> Meanwhile, their high energy production cost and the inconveniences due to their rigid and heavy property retards the growth of PV electricity supply. To breakout this issue, the development of thin film PV produced by inexpensive ways such as solution process is needed. In terms of stability, inorganic or organic/inorganic hybrid devices appear to be promising. In this chapter, the recent progress, principle, and underlying problems of hybrid thin film solar cells are reviewed.



**Figure 1-1.** One of future scenario of global energy supply reported in World Energy Assessment.<sup>1</sup>

## 1-1. Hybrid thin film solar cells

Organic/inorganic hybrid thin film solar cells (HSCs) have shown much interest owing to their rapid growth of power conversion efficiency (PCE). The beginning point of HSCs development turns back to the reports of the first organic solar cells demonstrated by C. W. Tang (1%, in 1986)<sup>4</sup> and the outperforming dye-sensitized solar cell (DSSC) demonstrated by M. Grätzel, *et al.* (7.9%, in 1991)<sup>5</sup>. Thereafter, the use of inorganic quantum dots (QDs) as a sensitizer allowed to convert DSSC using electrolyte into all solid HSCs. Conjugated molecules were used instead of an electrolyte to extract photogenerated holes.<sup>6</sup> In 2009, T. Miyasaka, *et al.* firstly reported lead halide perovskite (LHP)-based DSSC with the PCE of 3.8%.<sup>7</sup> Afterward, Park, *et al.* succeeded to fabricate an all solid perovskite solar cell, significantly promoted further investigation of perovskite solar cells.<sup>8</sup> In 2020, HSCs such as perovskite solar cells and QDs (PbS) solar cells achieved exceptionally high PCE over 25% and 11.5%, respectively (Figure 1-2.).<sup>3,9</sup>

Although all inorganic and organic PVs are also notable, HSCs have some superior points. Because solution process is available in the production, HSCs is expected to be less expensive than inorganic PVs. As for air stability, organic PVs suffer from oxidation, which significantly quenches the photogenerated exciton.<sup>10</sup> Whereas in HSCs, organic materials such as conjugated polymers are mostly used to extract holes from light absorbing layer, where oxidation induces *p*-type doping increasing hole mobility.<sup>11–13</sup> These properties further enhance the possibility of HSCs (especially perovskite) as next generation solar cells.



Figure 1-2. Recent progress of emerging thin film solar cells.<sup>3</sup>

## 1-2. Fundamental of solar cells

#### 1-2-1. Photoelectric conversion principle

The *n-i-p* structure is the most common architecture of HSCs (Figure 1-3a),<sup>14–18</sup> in which a light absorber (*i* layer) is sandwiched by electron transport material (ETM; *n* layer) and hole transport material (HTM; *p* layer), with electrodes as bottom and top electric contact layer. A transparent electrode, located at the bottom, such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) is used to introduce light into a device. Upon the light irradiation, electrons are excited in the *i* layer to form excitons. When inorganic material or hybrid perovskite is used as the *i* layer, the excitons immediately separate into free electrons and holes at room temperature.<sup>19,20</sup> The free electrons and holes are transported to ETM and HTM respectively, and then captured by the electrodes. For an efficient electron transfer to ETM, the conduction band minimum (CBM) of the *i* layer should be shallower than that of ETM (Figure 1-3b). Mesoporous ETM such as TiO<sub>2</sub> (mp-TiO<sub>2</sub>) is commonly used in regular cells to enhance electron extraction.<sup>21–23</sup> Of course, the valence band maxima (VBM) of *i* layer should be deeper than that of HTM for proper hole extraction.



**Figure 1-3.** (a) Schematic image of the structure of *n-i-p* thin film solar cell. (b) Energy diagram of *n-i-p* solar cells. (c) Shockley-Queisser limit for the PCE of a solar cell obtained from approximated solar spectrum.<sup>24</sup>

The selection of light absorber with optimal bandgap is of critical importance in development of efficient solar cells. Because the photoelectric output power is the product of current and voltage, where these are in a trade-off relation in terms of bandgap, the moderate bandgap is required. According to Schockley-Queisser limit, 1.34 eV of bandgap is the most optimal under AM1.5G<sup>24</sup> (Figure 1-3c). Other important factors such as charge separation are mentioned later.

#### 1-2-2. How to evaluate solar cells

Current-voltage (*JV*) characteristics of a solar cell is evaluated by plotting the measured current density under the pseudo sunlight (AM1.5G) as a function of applied voltage. Digital multi meter is used to measure the electrical output from a solar cell along with scanning the value of applied voltage. When the bias is scanned from a low to high voltage, it is called as forward scan. On the other hand, the bias scan from high to low voltage is called as reverse scan. The *JV* curve as represented in Figure 1-4a is obtained after the scanning. The performance parameters found from the *JV* curve are the short circuit current (*J*<sub>SC</sub>), open circuit voltage (*V*<sub>OC</sub>), and fill factor (FF), where *J*<sub>SC</sub> and *V*<sub>OC</sub> are the current density and voltage at 0 output obtained from the crossing points of *JV* curve and the two axes, FF is the maximum output power (*J*<sub>Max</sub> × *V*<sub>Max</sub>) divided by *J*<sub>SC</sub> × *V*<sub>OC</sub>. The details of each parameter will be discussed in the following section. The power conversion efficiency (PCE) is obtained as the product of these parameters (PCE = *J*<sub>Max</sub> × *V*<sub>Max</sub> = *J*<sub>SC</sub> × *V*<sub>OC</sub> × FF).

The JV curve is rationally represented via following Shockley diode equation:

$$J_d = J_0 \{ \exp\left(\frac{eV_d}{nkT}\right) - 1 \}$$
(1-1)  

$$J = J_{SC} - V_d / R_{sh} - J_d$$
(1-2)  

$$V = V_d + JR_S$$
(1-3)

, where  $J_0$  is the saturation current, *e* is the elemental charge,  $J_d$  and  $V_d$  are the current density and voltage across the diode, *n* is the ideal factor, *k* is Boltzmann constant, *T* is temperature,  $R_{\rm sh}$  and  $R_{\rm s}$  are the shunt and series resistance of device, as represented in Figure 1-4b.  $R_{\rm sh}$  and  $R_{\rm s}$  are also approximately calculated as  $(-dJ/dV)^{-1}$  at V = 0 and  $V_{\rm OC}$ , respectively. The fitting parameters *n*,  $R_{\rm sh}$ , and  $R_{\rm s}$  are of use in the detailed discussion of JV characteristics along with  $J_{\rm SC}$ ,  $V_{\rm OC}$ , and FF.

The external quantum efficiency (EQE) spectra is also obtained from solar cells by plotting the current density as a function of irradiated light wavelength. The integration of current density with respect to the wavelength generally coincides with the  $J_{SC}$  obtained in JV measurement.



Figure 1-4. (a) Schematic image of JV curve and calculation of PCE. (b) Equivalent circuit of the measurement system of solar cells.

#### 1-2-3. Physical meaning of the parameters

Here, the physical sense of JV characteristic parameters, J<sub>SC</sub>, V<sub>OC</sub>, FF, R<sub>sh</sub>, R<sub>s</sub>, and n are discussed.  $J_{SC}$  is basically represented as the product of absorbed photon density, charge separation efficiency, and charge extraction efficiency. Thus, narrow bandgap and high absorption coefficient affords a high  $J_{SC}$  value. For an efficient charge separation, quantum confined structure is not preferred. For an efficient charge extraction, a long charge diffusion length and smooth interfacial charge transport is required. Voc is determined by the bandgap of absorber and the energy losses, which are attributed to bulk and interfacial recombination. To distinguish the bulk and interfacial effect, temperaturedependent  $V_{OC}$  measurement could be one of ways.<sup>25,26</sup> FF is directly affected by  $R_{sh}$  and  $R_{\rm s}$ , where both increment of  $R_{\rm sh}$  value and decrement of  $R_{\rm s}$  value enhance FF. The small  $R_{\rm sh}$  represents high recombination rate or existence of leak current due to poor coverage of certain layer in PV device,  $^{27,28}$  meanwhile the large  $R_s$  represents the high resistance for photogenerated electrons and holes. Low charge mobility and high interfacial resistance induce the increase of  $R_{s}$ .<sup>27,29</sup> n (ideal factor) value, usually between 1 and 2, is related with charge recombination mode. n = 1 indicates a band-to-band recombination dominated mode, whereas n = 2 indicates a gap state assisted recombination dominated mode.<sup>28</sup>

## 1-3. Lead Halide Perovskites (LHPs)

#### 1-3-1. Photovoltaic performance of LHPs

LHPs consisting of A-site cation (Cs<sup>+</sup>, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (MA<sup>+</sup>), and HC(NH<sub>2</sub>)<sup>+</sup> (FA<sup>+</sup>)), Bsite metal (Pb), and X-site halogen (I, Br, and Cl) (Figure 1-5a) have almost ideal physical characters, such as large absorption coefficient throughout visible region,<sup>30</sup> low exciton binding energy,<sup>31</sup> high electron and hole mobilities,<sup>32,33</sup> and polaron formation preventing recombination.<sup>34</sup> The PCE of perovskite solar cells have been dramatically increased from 3.8% in 2009 (first report by T. Miyasaka, *et al.*) to 25.5% in 2020, near to the best PCE of single crystalline Si solar cells.<sup>3,7</sup> In addition, their production cost is expected much lower than those of crystalline Si solar cells owing to the solution process. LHP thin films are fabricated by facial spin-coating of the precursor solution including AX and PbX<sub>2</sub>, followed by thermal annealing. Besides, the high emission property of Br-exchanged perovskite such as methylammonium lead bromide (MAPbBr<sub>3</sub>) is beneficial in photonic applications such as laser and light emitting diode (LED).<sup>35,36</sup>



**Figure 1-5.** (a) The image of crystal structure of ABX<sub>3</sub> LHPs, and (b) the electronic structure of MAPbI<sub>3</sub>

The outstanding performance of perovskite solar cells is originated from their electronic structure. As shown in Figure 1-5b, the CBM of MAPbI<sub>3</sub> is the hybrid of Pb 6p, I 5s, and I 5p, whereas the VBM is consists of Pb 6s and I 5p.<sup>37–39</sup> This configuration affords spherically symmetric wave function of CBM and VBM with the inverted parity each other, resulting in isotropic charge transfer and strong absorption. Furthermore, the anti-bonding nature of VBM inhibits the generation of deep defect level inside the gap.<sup>40</sup> This is a notable superiority of LHPs to inorganic QDs, considering their intrinsically numerous surface defect due to a huge surface area.

#### 1-3-2. Stability and toxicity of LHPs

The stability of LHPs in humid condition is much lower than typical inorganic semiconductors such as Si. LHPs easily adsorb H<sub>2</sub>O molecules, and dissociate into PbI<sub>2</sub> and AI (A = Cs, MA, FA) or transform into the complex of LHPs and water.<sup>41–43</sup> The degradation can be detected by the changing in the thin film color into PbI<sub>2</sub>-originated yellow color appeared after air exposure (Figure 1-6). Their thermal stability is also in concern.<sup>44,45</sup> Organic components in LHPs such as MA and FA gradually sublimate or dissociate into other molecules at high temperature. Thus, the long-term stability of LHPs remains a matter of ongoing investigation.

The high toxicity of LHPs along with their high solubility in water is also seriously concerned.<sup>46</sup> It is not only environmental but also economic disadvantage, requiring proper regulation throughout their product life. In Europe, the use of lead in electronic devices are strictly limited by RoHS compliant. The rules to limit harmful materials appear to become further rigorous. In this viewpoint, the development of Pb-free perovskites or analogous semiconductors has great potential to make a leap in the production of ideal solar cell.



Figure 1-6. The pictures of LHP thin films with air exposure time.

#### 1-3-3. Tin halide perovskites (THPs)

THPs have been emerged as environmental friendly Pb-free perovskites.<sup>47–49</sup> They have a relatively narrow bandgap compared to LHPs, close to the Shockley-Queisser optimal bandgap.<sup>50</sup> Theoretical calculation implies that hole effective masses in THPs is intrinsically smaller than those of LHPs.<sup>51</sup> However,  $\text{Sn}^{2+}$  ions in THPs suffers from significant oxidation to yield  $\text{Sn}^{4+}$ , forming a deep electron trap level.<sup>52–57</sup> The instability of  $\text{Sn}^{2+}$  ion is intrinsically originated from the lack in inert pair electron effect. Due to the weak stabilization of the 5s<sup>2</sup> unshared electron pair in Sn(II), the electron pair is easily lost, yielding Sn(IV). The contamination of oxidized species is considered to occur throughout the all processes including row material production, device fabrication, and device evaluation. The dark carrier density of THPs ( $10^{17}-10^{19}$  cm<sup>-3</sup>) inherently doped by conversion from  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  is many orders of magnitude higher than that of MAPbI<sub>3</sub> ( $10^9-10^{11}$  cm<sup>-3</sup>),<sup>58,59</sup> which causes charge recombination, shorting of the diode circuit, and deterioration of the open-circuit voltage.<sup>60–62</sup> Due to these natures, the reported best PCE of THP solar cell (~13%, in 2020) is much lower than that of LHP,<sup>63</sup> even be measured in N<sub>2</sub> atmosphere.

## 1-4. Bi- and Sb-based semiconducting materials

#### 1-4-1. Various Bi- and Sb-based materials

Another choice for Pb-free solar cells is the use of bismuth (Bi) and antimony (Sb) instead of Sn.<sup>64–68</sup> The electronic configurations of Bi<sup>3+</sup> and Sb<sup>3+</sup> ion of  $6s^26p^0$  and  $5s^25p^0$ , which are analogous to those of Pb<sup>2+</sup> and Sn<sup>2+</sup>, would yield similar optoelectronic characters with LHPs such as high absorption coefficient, high charge mobility, and inhibited defect level. The heavy atom effect, which promotes efficient absorption,<sup>66</sup> is also expected. In addition, elementally abundant, non-toxic Bi and Sb are advantageous over commercialized inorganic solar cells<sup>69</sup> such as CdTe<sup>70</sup> and CIGS (Cu-In-Ga-S/Se)<sup>71</sup>, as well as emerging LHP solar cells.<sup>3</sup>

Meanwhile, unlike Sn, 3-valent cationic nature of Bi and Sb disenable the straightforward substitution of  $Pb^{2+}$  ion in LHPs. Thus, alternative crystal structures instead of ABX<sub>3</sub> need to be explored. The representative structures of Bi- and Sb-based semiconducting materials are summarized in Figure 1-7. A<sub>3</sub>B<sub>2</sub>X<sub>9</sub> (A = Cs<sup>72</sup> MA,<sup>72</sup> FA,<sup>73</sup> B = Bi,<sup>72</sup> Sb,<sup>74,75</sup> X = I,<sup>72</sup> Br<sup>76</sup>) type materials with 0-dimensional dimeric or 2-dimensional layered structure are widely studied (Figure 1-7a). These are easily fabricated through the simple spin-coating of the solution of AX and BX<sub>3</sub> dissolved in dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF). The silver-bismuth-iodide Ag<sub>x</sub>Bi<sub>(1-x)</sub>I<sub>(3-2x)</sub> with cubic and layered structures (Figure 1-7b),<sup>77-79</sup> where the structure type (cubic or layered) is controlled by Ag:Bi ratio and the 3-dimensional double perovskite (DP), where Ag and Bi are alternately locating in B-site (Figure 1-7c)<sup>80-82</sup> have been also emerged as solution-processable Bi and Sb halide semiconductors.

Besides, chalcogenides such as  $Bi_2Te_3$ ,  $Bi_2S_3$ ,  $Sb_2S_3$ ,  $AgBiS_2$  and  $CuBi(Sb)S_2$  are known as typical semiconducting materials (Figure 1-7d).<sup>83–90</sup> Photodetectors using  $Bi_2Te_3^{87-89}$  show notable photosensitivity, and  $Bi_2S_3$  including elementally-abundant sulfur instead of tellurium is used as the photoabsorber of QDs solar cell with the PCE of 0.46%.  $Sb_2S_3$  have been widely studied owing to their particularly high PCE (~7.5%).<sup>90</sup> The chalcohalides including both chalcogen and halogen such as SbSeI and MASbSI<sub>2</sub> are also notable candidates (Figure 1-7e, f).<sup>91,92</sup> For instance, Nie *et al.* reported a PCE of over 3% for MASbSI<sub>2</sub> and SbSI solar cell.<sup>92,93</sup> Quantum chemical calculation predicted the light effective masses of the hole and electron in MASbSI<sub>2</sub>.<sup>94</sup> The reported PCEs of solar cells using these materials are summarized in Table 1-1. The PCEs are varying from 0.012% to 7.1% depending on the active layer.

The confusing matter is the way to select the plausible one from these numerous candidates without any overlooking. The device evaluation definitely includes the contact

issues at the semiconductor/electrode interfaces, precluding the direct observation of charge carrier dynamics. For proper material exploration, it is essential to investigate materials from viewpoints of their fundamental optoelectronic properties such as energy level of VBM and CBM, charge diffusion, and interfacial transport property.



**Figure 1-7.** Crystal structures of Bi- and Sb-based solar absorbers: (a)  $A_3M_2X_9$  (dimer or layered), (b)  $Ag_xBi_{(1-x)}I_{(3-2x)}$  (layered or rod), (c)  $A_2MM'X_6$  (double perovskite: DP), (d)  $M_2S_3$  (layered), (e) MSX (rod-like), and (f) AMSX<sub>2</sub> (split anion perovskite: SAP).

device structure	PCE (%)	Ref
FTO/cTiO2/mpTiO2/Cs3Bi2I9/Spiro-OMeTAD/Au	1.09	72
$FTO/cTiO_2/mpTiO_2/MA_3Bi_2I_9/Polyindenofluoren-$	0.71	95
8-triarylamine/Au		
FTO/TiO <sub>2</sub> /BiOI (photoanode), Pt/FTO (cathode),	1.03	96
$I_3^-/I^-$ (redox electrolyte)		
FTO/BiSI/CuSCN/Pt,FTO	0.012	97
ITO/Bi <sub>2</sub> S <sub>3</sub> /P3HT/Ag	0.46	98
FTO/TiO <sub>2</sub> /AgI,BiI <sub>3</sub> (AgI:BiI <sub>3</sub> =2:1)/P3HT/Au	2.1	78
ITO/SnO <sub>2</sub> /AgBiI <sub>4</sub> /PTAA/Au	2.8	99
FTO/cTiO2/mpTiO2/Cs2AgBiBr6/PTAA/Au	1.26	100
ITO/ZnO/AgBiS2 QDs/PTB7/MoO <sub>X</sub> /Ag	6.3	101
ITO/PEDOT:PSS/Cs3Sb2I9/PCBM/C60,BCP/Au	0.84	74
ITO/PEDOT:PSS/MA3Sb2I9/PCBM/C60,BCP/Au	2.04	74
FTO/cTiO2/mpTiO2/SbSI/PCPDTBT/PEDOT:PSS	2.05	93
/Au	5.05	
FTO/cTiO2/mpTiO2/Sb2S3/Spiro-OMeTAD/Au	7.5	90
FTO/cTiO2/mpTiO2/MASbSI2/PCPDTBT	3.08	92
/PEDOT:PSS/Au		
	device structure FTO/cTiO2/mpTiO2/Cs3Bi2I9/Spiro-OMeTAD/Au FTO/cTiO2/mpTiO2/MA3Bi2I9/Polyindenofluoren- 8-triarylamine/Au FTO/TiO2/BiOI (photoanode), Pt/FTO (cathode), I3 <sup>-</sup> /I <sup>-</sup> (redox electrolyte) FTO/BiSI/CuSCN/Pt,FTO ITO/Bi2S3/P3HT/Ag FTO/TiO2/AgI,BiI3(AgI:BiI3=2:1)/P3HT/Au ITO/SnO2/AgBiI4/PTAA/Au FTO/cTiO2/mpTiO2/Cs2AgBiBr <sub>6</sub> /PTAA/Au ITO/ZnO/AgBiS2 QDs/PTB7/MoO <sub>X</sub> /Ag ITO/PEDOT:PSS/Cs3Sb2I9/PCBM/C60,BCP/Au ITO/PEDOT:PSS/MA3Sb2I9/PCBM/C60,BCP/Au FTO/cTiO2/mpTiO2/Sb2S3/Spiro-OMeTAD/Au FTO/cTiO2/mpTiO2/Sb2S3/Spiro-OMeTAD/Au FTO/cTiO2/mpTiO2/MASbSI2/PCPDTBT /PEDOT:PSS/Au	device structure         PCE (%)           FTO/cTiO2/mpTiO2/Cs3Bi2I9/Spiro-OMeTAD/Au         1.09           FTO/cTiO2/mpTiO2/MA3Bi2I9/Polyindenofluoren- 8-triarylamine/Au         0.71           FTO/TiO2/BiOI (photoanode), Pt/FTO (cathode), I3 <sup>-</sup> /I <sup>-</sup> (redox electrolyte)         1.03           FTO/BiSI/CuSCN/Pt,FTO         0.012           ITO/Bi2/Sa/P3HT/Ag         0.46           FTO/TiO2/AgI,BiI3(AgI:BiI3=2:1)/P3HT/Au         2.1           ITO/SnO2/AgBiI4/PTAA/Au         2.8           FTO/cTiO2/mpTiO2/Cs2AgBiBr <sub>6</sub> /PTAA/Au         1.26           ITO/PEDOT:PSS/Cs3Sb2I9/PCBM/C60,BCP/Au         0.84           ITO/PEDOT:PSS/MA3Sb2I9/PCBM/C60,BCP/Au         2.04           FTO/cTiO2/mpTiO2/Sb2S/Spiro-OMeTAD/Au         3.05           /Au         7.5           FTO/cTiO2/mpTiO2/Sb2S/Spiro-OMeTAD/Au         7.5           FTO/cTiO2/mpTiO2/Sb2S/Spiro-OMeTAD/Au         7.5           FTO/cTiO2/mpTiO2/Sb2S/Spiro-OMeTAD/Au         7.5           FTO/cTiO2/mpTiO2/MASbSI2/PCPDTBT         3.08           /PEDOT:PSS/Au         3.08

**Table 1-1.** Summary of reported PCEs or the solar cells using Bi- and Sb-based materials.

#### 1-4-2. Thin film preparation process

On one hand, halide materials such as A<sub>3</sub>B<sub>2</sub>X<sub>9</sub>, AgBiI, and A<sub>2</sub>BB'X<sub>6</sub> are prepared by facial spin-coating of precursor solution and subsequent thermal annealing. On the other hand, such a simple process is not applicable for the preparation of chalcogenide and chalcohalide thin films due to their limited solubility in organic solvent. The typical deposition processes of chalcogenide thin films are chemical bath deposition (CBD),<sup>102</sup> deposition,<sup>98,101</sup> successive-ionic-layer-adsorption-reaction nanoparticles (NP) (SILAR),<sup>96,103</sup> and spray pyrolysis (SP)<sup>104</sup>. The CBD is a way to gradually deposit metal chalcogenide film onto the substrate through the reaction of metal cation and chalcogen anion (Figure 1-8a). The repeated spin-coating of colloidal NPs suspension, followed by ligand exchange is a typical NPs deposition way (Figure 1-8b). In the successive-ioniclayer-adsorption-reaction (SILAR), thin films are made by immersing a substrate into the solution of metal cation and chalcogen anion alternately (Figure 1-8c). The SP is conducted by spraying precursor solution including metal and sulfur source onto a heated substrate to induce thermal decomposition (Figure 1-8d). These methods mostly afford smooth films, though with relatively small grain size compared to those of LHPs (0.5~1 μm). The small grain size is detrimental to charge separation and transport, due to the strong confinement effect and the formation of extensive grain boundaries. Furthermore, recent studies exploited facile methods consisting of the spin-coating of precursor solution including metal and sulfur source, followed by thermal decomposition (Figure 1-8e). Metal-salts/thiourea complex and metal-ethylxanthate were mostly used as the precursors.<sup>84,105,106</sup> In Bi<sub>2</sub>S<sub>3</sub> film preparation, the use of metal-ethylxanthate yields large grain size of ~0.5µm, comparable to those of LHPs.<sup>105</sup> The remaining issues to be overcame are generation of film roughness with numerous pin-holes.<sup>105,106</sup>

The preparation methods of chalcohalide films were recently reported. Sfaelou, *et al.* demonstrated the preparation of BiOI thin film by the SILAR method.<sup>95</sup> Nie, *et al.* reported that 2-step fabrication of SbSI consisting of Sb<sub>2</sub>S<sub>3</sub> deposition by CBD and following repeated spin-coating of SbI<sub>3</sub> solution followed by thermal annealing afforded improvement of PCE up to 3% (Figure 1-8f).<sup>93</sup> Meanwhile, Hahn, *et al.* successfully prepared a BiSI film by facile 1-step method including the spin-coating of precursor solution containing Bi(NO<sub>3</sub>), NH<sub>4</sub>I, and thiourea, followed by thermal decomposition.<sup>97</sup> The development of 1-step preparation method for outperforming Sb-based chalcohalides is definitely one of the ways to improve lead free solar cells.



**Figure 1-8.** The schematics of Bi and Sb chalcogenide and chalcohalide thin film preparation methods; (a) CBD, (b) NPs deposition, (c) SILAR, (d) spray pyrolysis, (e) thermal decomposition of precursor, and (f) 2-step coating method of SbSI via CBD and SbI<sub>3</sub> spin-coating.<sup>93</sup>

## 1-5. Time-Resolved Microwave Conductivity (TRMC)

Existence of the contact issue makes the direct observation of charge carrier dynamics such as mobility, lifetime, and charge transport to adjacent layer quite unreliable in device evaluation. Thus, contact-free measuring technique is desired. Time-resolved microwave conductivity (TRMC) measurement is a powerful way to measure transient conductivity ( $\Delta \sigma$ ) upon pulse light irradiation because detection by microwave in TRMC can exclude undesired contact resistance and capacitance. Also, the use of alternated electric field induces local vibration of charge carriers. This enables intrinsic evaluation of charge carrier dynamics suppressing the trapping effect, which mostly appears in contacted measurement.

In the measurement, film samples deposited on a quartz substrate or powder attached on quartz with tape are set in a resonant cavity to irradiate microwave and pulsed light. Under the resonant state,  $\Delta \sigma$  is obtained via following equation:

$$\Delta \sigma = \frac{1}{A} \frac{\Delta P_r}{P_r} \tag{1-4}$$

, where A is the sensitivity factor,  $P_r$  is the reflected microwave from the sample,  $\Delta P_r$  is the transient  $P_r$  value with pulse irradiation.  $\Delta \sigma$  is also described as follows:

$$\Delta \sigma = en\Sigma \mu = eF\phi\Sigma \mu \qquad (1-5)$$

, where *e* is the elementary charge, *n* is the density of photogenerated charge carriers,  $\Sigma \mu$  is the sum of charge carrier mobilities, *F* is the correction factor that includes the absorbed photon density, and  $\phi$  is the quantum efficiency of the charge carrier generation. When a laser is used as the light source,  $\phi \Sigma \mu$  is mostly used instead of  $\Delta \sigma$ .

Here, the important features of TRMC is as follows: i) Intrinsic charge carrier dynamics is evaluated by excluding the effects of contact and significant trapping effect. ii) Owing to the rapidness of sample preparation and measurement, large scale screening is possible. iii) It is possible to reveal the charge transfer between two layers via the measurement of multilayered samples. Given these properties, numerous Bi- and Sb-based materials were investigated by TRMC.

#### 1-6. Outline of This Work

In this dissertation, the author presents new insights into the molecule-induced transformation properties of LHPs and THPs, and the optoelectronic properties of Bi- and Sb-based semiconductors as alternative absorber. It has been known that metal halide perovskites are degraded in ambient condition through the deformation of crystal structure and chemical doping. However, the detailed understanding of how their optoelectronic nature change is still an ongoing mater. The next chapter reveals the oxidation effect on the physical properties of THPs and the anomalous thermoresponsive emission behavior of LHPs nanoparticles.

The following chapters are regarding the exploration of Bi- and Sb-based materials. Motivated by the instability and toxicity of LHPs and THPs, the author focused on Bi, and subsequently on Sb. Although there are several reports on Bi- and Sb-based materials, comprehensive evaluation of these materials are still lacking. Besides, the development of solution-based thin film fabrication process is also a remaining task. In Chapter 3, invention of a new fabrication process of Bi<sub>2</sub>S<sub>3</sub> thin film is presented, which increases charge mobility with low dark current. The works described in Chapter 4 and 5 are comprehensive investigation of Bi- and Sb-based materials having various structures. The contents of each chapter are outlined as follows.

In *Chapter 2*, the transformation properties of THPs and LHPs induced by molecular adsorption are presented. Firstly, the effect of air exposure on THPs were studied using TRMC and photoelectron yield spectroscopy (PYS). Time-dependent measurement with minute-scale interval elucidated the changing of photoconductivity and energy level as a function of air exposure time. The effect of the composition of THPs and additives are also revealed. Secondly, the new temperature-dependent luminescence property of LHPs nanoparticles (NPs) was discovered. The addition of methylamine (CH<sub>3</sub>NH<sub>2</sub>) on NPs colloidal solution induced lowest solution critical temperature (LCST) behavior, where NPs dissolves in solution at low temperature, whereas they appear at high temperature. Lastly, based on optical and structural analysis, the mechanism of the phenomena was successfully provided.

In *Chapter 3*, the development of a new fabrication process of Bi<sub>2</sub>S<sub>3</sub> thin film with high charge mobility is described. Among TRMC screening of inorganic semiconductors, Bi<sub>2</sub>S<sub>3</sub> powder was found to show extremely high photoconductivity. However, Bi<sub>2</sub>S<sub>3</sub> thin films prepared by previous methods such as NPs deposition, CBD, etc. showed significantly low photoconductivity or large dark current, resulting in small light/dark current ratio. By focusing on crystal growth, the author established the new process for preparation of Bi<sub>2</sub>S<sub>3</sub> film with large crystal grain and high purity. The obtained film exhibited 460 of light/dark current ratio under AM 1.5G, 6~420-fold larger than those of the films prepared by previous methods.

In *Chapter 4*, the comparative study of the charge carrier dynamics of Bi-based halide dimer  $A_3Bi_2I_9$  (A = Cs, MA, FA) and double perovskite  $Cs_2AgBiBr_6$  based on TRMC evaluation were presented. The evaluation of single layer of absorber and multilayer such as ETM/Absorber provides the insights into interlayer charge transport. Although  $Cs_2AgBiBr_6$  afforded superior charge transport, the charge extraction is assumed to be still insufficient, due probably to low charge separation efficiency. This is considered as the origin of the limited current density of  $A_3Bi_2I_9$  and  $Cs_2AgBiBr_6$  solar cells.

In *Chapter 5*, it is described that comprehensive evaluation of Bi- and Sb-based materials with 44 compositions were performed. The crystal structure formation, energy level, photoconductivity, and interlayer transport property were revealed by XRD, PYS, photoabsorption spectroscopy, and TRMC. Interestingly, several Sb-based materials such as SbSI, Sb<sub>2</sub>S<sub>3</sub>, AgSbI<sub>4</sub>, and MASbSI<sub>2</sub> showed remarkable increase in photoconductivity by combining with TiO<sub>2</sub>. This is considered as a result of efficient electron transfer. It was also revealed that the inclusion of thiophene unit in HTM affords highly improved interlayer hole transport. Finally, SbSI-based solar cells showed the highest PCE of 2.91% under AM 1.5G, which is notably high among solution processed Bi- and Sb-based solar cells.

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## **Chapter 2: Transformation Mechanism of Pb and Sn Perovskite via Molecular Adsorption and Evolution for PL Switching**

#### 2-1. Introduction

The problem lying on both of LHPs and THPs is their instability in the air. It has been known that methyl ammonium lead iodide (MAPbI<sub>3</sub>) suffers gradual deterioration within a few days in humidity.<sup>1</sup> Meanwhile, the oxygen-induced degradation in THPs is more serious. Because the addition of SnF<sub>2</sub> to CsSnI<sub>3</sub> was found to mitigate the initial *p*-doping,<sup>2</sup> a relatively large amount of SnF<sub>2</sub> (10–20 mol %) is mixed with MASnI<sub>3</sub> or formamidinium-cation- [HC(NH<sub>2</sub>)<sup>2+</sup>-, FA-) based FASnI<sub>3</sub>, exhibiting PCEs of 2–6%.<sup>3,4–8</sup> However, the dark carrier density is still high even after SnF<sub>2</sub> addition (~10<sup>17</sup> cm<sup>-3</sup>),<sup>4,9</sup> and the mechanism remains poorly understood.

In the first half of this chapter, the author presents the electrochemical and optoelectronic properties of MASnI<sub>3</sub> and FASnI<sub>3</sub> with/without SnF<sub>2</sub> additive. These properties were systematically evaluated using the photoelectron yield spectroscopy (PYS)<sup>10</sup> and laser flash-photolysis time-resolved microwave conductivity (TRMC),<sup>11,12</sup> particularly regarding the effect of air exposure. With the use of PYS and TRMC, the change in the valence band maxima (VBM) level and the transient conductivity is evaluated. PYS is a type of ultraviolet photoelectron spectroscopy (UPS) that records the photocurrent extracted under a relatively high extraction voltage (10–100 V) upon UV irradiation (shorter than 310 nm). Consequently, it allows for the evaluation of a wide range of samples including thick films and powders in a vacuum and even in air. The author performed PYS and TRMC measurements of powder samples instead of thin film samples to retard degradation process. The observed shift in VBM (PYS) and decrease of transient conductivity (TRMC) are important when designing the device structure of a THP solar cells and in deepening the understanding of the degradation process.

As for LHPs, the high humidity induces the irreversible formation of LHPs-H<sub>2</sub>O complex, resulting in the degradation. Meanwhile, the phase transition induced by methylammonium (CH<sub>3</sub>NH<sub>2</sub>) gas is reversibly occurred in room temperature.<sup>13</sup> Given the specific interaction between LHP and CH<sub>3</sub>NH<sub>2</sub>, the latter half of this chapter regards to an unprecedented lower critical solution temperature (LCST) for methylammonium lead bromide (MAPbBr<sub>3</sub>) nanoparticle (NP) colloidal solution with the presence of CH<sub>3</sub>NH<sub>2</sub>. This implies the possibility of controlling the crystal structure and chemical compositions

through external stimulation such as temperature, which may enable reversible switching of emission property. On the other hand, aqueous polymer solutions represented by poly(N-isopropylacrylamide) (PNIPA) are known to exhibit a temperature-triggered coil–globule transition, which leads to a lower critical solution temperature (LCST).<sup>14</sup> Through dipole–dipole and hydrogen-bonding interactions in water, PNIPA is hydrated below a cloud point ( $T_C \approx 32$  °C), but becomes shrunken and precipitates through the liberation of hydrated water molecules above this temperature.<sup>15,16</sup> It is the low dissolution entropy of the polymer that is responsible for this reversible conformational change, thus making similar behavior a rarity in molecular or inorganic materials due to the fact that a high entropy at high temperatures tends to favor dissolution. Particularly, a luminescent LCST system that is truly made of "molecules" or "ions" has never yet been achieved.

In this chapter, it is presented what is believed to be the first example of LCST behavior in LHP NPs that not only involves a transition between solution and suspension but also photoemission switching between blue (430 nm) and green (525 nm). A reversible LCST has been achieved by adding a few amounts of CH<sub>3</sub>NH<sub>2</sub> found to facilitate the formation and decomposition of perovskite NPs at the desired temperature (30-80 °C). These compounds are neutral/ionic molecules (e.g., CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) and metal/halogen ions (Pb<sup>2+</sup>, Br<sup>-</sup>) that have atomic (molecular) weights of less than three hundred. The self-organization of organic–inorganic species in nonpolar solvent, which is mediated by an intermediate 1D crystal, was also found to have a marked effect on the thermoresponsive phenomenon, thus making it distinctly different to conventional LCST mechanisms based on the hydration and dehydration of polymers or molecules.

## 2-2. Results and Discussion

#### 2-2-1. Energetics of THPs Studied Using PYS

The PYS spectra of MASnI<sub>3</sub> without air exposure exhibit a distinct rise of the form (yield)1/n, where the onset positions are mostly unchanged by the addition of 20 mol %  $SnF_2$  (Figure 2-1a). Generally, n = 3 is used for semiconductors,  $^{17,18}$  whereas n = 2 is used for metals.<sup>19</sup> This empirical power law is inferred from the results of vibrational transition probabilities and surface transmission probabilities.<sup>20</sup> In the present analysis, n = 3 was used, which affords a good linear fitting for the base and the increase to calculate the onset that corresponds to the VBM. (The use of n =2 deepens the VBM by approximately 0.05 eV.) With increasing air exposure time, the yields gradually decrease, and onsets become unclear. the The degradations of the PYS spectra are almost the same between MASnI3 and FASnI<sub>3</sub> (Figure 2-1b).



**Figure 2-1.** PYS spectra of (a) MASnI<sub>3</sub> (solid circles) and MASnI<sub>3</sub> + SnF<sub>2</sub> (open circles), and (b) FASnI<sub>3</sub> (solid circles) and FASnI<sub>3</sub> + SnF<sub>2</sub> (open circles). Solid lines are linear fittings without (black) and with (gray) 20 mol% SnF<sub>2</sub>. Each line was determined as the pair of a base and a rise to calculate an onset (= VBM).

The VBMs of the THPs are plotted as functions of the air exposure time (Figure 2-2a). The VBM of MASnI<sub>3</sub> is  $-5.02 \pm 0.03$  eV, as averaged among the short air exposure times. The value is unlikely to be affected by the addition of SnF<sub>2</sub> ( $-5.00 \pm 0.03$  eV), whereas the downward shift of the VBM (e.g.,  $-5.17 \pm 0.04$  eV at 18 min) owing to the degradation in air is slightly moderated by SnF<sub>2</sub> ( $-5.08 \pm 0.03$  eV at 18 min). The shift is accompanied by a decrease of the rise slope (Figure 2-2b), which makes the onset unclear after longer than 20 min. The VBM of lead-based MAPbI<sub>3</sub> powder evaluated using the same instrument is  $-5.45 \pm 0.05$  eV, which is consistent with those of other studies (from -5.40 to -5.50 eV).<sup>21-24</sup> However, the obtained VBM of MASnI<sub>3</sub> lies between the reported values of  $-4.75^{25-27}$  and  $-5.47^{28,29}$  eV. According to the results of air exposure



**Figure 2-2.** (a) Dependence of the VBMs of MASnI<sub>3</sub> and FASnI<sub>3</sub> with/without SnF<sub>2</sub> on air exposure time. (b) Slopes of the rise (slope 1, solid symbols) and the base (slope 2, open symbols) obtained from the fitting of the PYS spectra in Figure 2-1. (c,d,e) Derivatives of the PYS spectra of (c) MASnI<sub>3</sub> and MASnI<sub>3</sub> + SnF<sub>2</sub>, (d) FASnI<sub>3</sub> and FASnI<sub>3</sub> + SnF<sub>2</sub>, and (e) MAPbI<sub>3</sub>. Solid circles and open squares represent air exposure times of 0 and 18 min, respectively. Insets are semilogarithmic plots of *dY/dhv* vs *hv*, which is indicative of the onset from -4.7 to -4.8 eV for the fresh (0-min) samples.

effects, degradation might be involved in the reported deep VBM (approximately -5.5 eV). This could be further linked to the formations of low-dimensional perovskite (MA<sub>2</sub>SnI<sub>6</sub>, analogous to Cs<sub>2</sub>SnI<sub>6</sub>)<sup>30,31</sup> having a deep VBM (vide infra) or O<sub>2</sub>/H<sub>2</sub>O adducts.<sup>32</sup> Indeed, the VBM of MASnI<sub>3</sub> at 28 min is deepened by 0.2 eV to -5.22 eV. In addition, the deformed curves cause an uncertainty of the onset (between -5.2 and -5.5 eV) that depends on the fitting range. FASnI<sub>3</sub> shows a similar behavior with respect to the shift of the VBM and the effect of SnF<sub>2</sub>. The initial VBMs of FASnI<sub>3</sub> without and with SnF<sub>2</sub> are mostly identical ( $-5.13 \pm 0.03$  and  $-5.12 \pm 0.03$  eV, respectively). They were shifted by approximately 0.2 eV to -5.38 eV (without SnF<sub>2</sub>) and -5.24 eV (with SnF<sub>2</sub>) at 18 min. The degradation is partly suppressed by SnF<sub>2</sub>, whereas the deformation of the curve of FASnI<sub>3</sub> is more obvious than that of MASnI<sub>3</sub> at 32 min. The VBM of FASnI<sub>3</sub> is also in the middle of the previously reported values ( $-4.7^{6,26}$  and  $-5.96^3$  eV).

The excessively low-lying VBM  $(-5.96 \text{ eV})^3$  is possibly explained by degradation as well. However, degradation alone is unable to account for the difference between the reported shallow VBM (-4.7 eV) and that of the fresh samples measured by the author (-5.0 eV).

For detailed discussion of electronic structures near the onsets of the PYS spectra, the author calculated the derivative of the photoelectron yield dY/dhv (hv is the photon energy in electronvolts), which is proportional to the effective density of the filled electronic states (density of states, DOS) near the band edge.<sup>33</sup> dY/dhv for MASnI<sub>3</sub> indicates a steep slope in the high-energy region (higher than 6.2 eV) and a less structured shoulder at 4.7–6.2 eV (Figure 2-2c). The shoulders (at 5.80 and 6.15 eV) are similar to those of BaTiO<sub>3</sub> and rubrene single crystals, the origins of which are the defect levels<sup>34</sup> and oxygen-related gap states,<sup>35</sup> respectively. The intensity of the shoulder was impeded by 20–30% upon the addition of SnF<sub>2</sub>, but the spectral features remained mostly unchanged. dY/dhv was drastically decreased by air exposure, together with an increase in the shoulder intensity relative to the high-energy region. The results imply that the addition of SnF<sub>2</sub> to MASnI<sub>3</sub> initially decreases the defect-related DOS to some extent, but that the electronic states are significantly altered by air exposure regardless of the presence of SnF<sub>2</sub>. After the oxidation, the shoulder became unclear, because it merged with the decreased main slope of the high-energy region.

Similarly, dY/dhv of FASnI<sub>3</sub> exhibited a clear shoulder with a single peak at ~6.15 eV; however, it disappeared upon mixing with SnF<sub>2</sub> (Figure 2-2d). This indicates that the initial defect-related DOS in FASnI<sub>3</sub> + SnF<sub>2</sub> is suppressed more effectively than that in MASnI<sub>3</sub> + SnF<sub>2</sub>, which is consistent with the superior PCE of the state-of-the-art FASnI<sub>3</sub> solar cell.<sup>4,6-8</sup> Notably, such a shoulder is also not observed for the outperforming MAPbI<sub>3</sub> (Figure 2-2e). Interestingly, the semilogarithmic plot of dY/dhv versus hv (insets in Figure 2-2c, d) gives an onset between -4.7 and -4.8 eV, which coincides with the reported VBMs of MASnI<sub>3</sub> (-4.75 eV)<sup>26,27</sup> and FASnI<sub>3</sub> (-4.70 eV).<sup>6,26</sup>

Figure 2-3a shows the XRD patterns of MASnI<sub>3</sub> and FASnI<sub>3</sub> with/without SnF<sub>2</sub>, which are identical to those of previous reports.<sup>3,4,32</sup> After 1 day of aging, the intensities were decreased for all of the samples, accompanying marginal shifts [e.g.,  $\pm 0.15^{\circ}$  for the (101) peak at  $2\theta \approx 14.2^{\circ}$ ; Figure 2-3b]. Note that the XRD measurements were performed in the air and that one scan took about 20 min, so that minute-scale degradation could not be evaluated. The changes in the XRD patterns are insignificant in comparison with those of previously reported spin-coated MA(FA)SnI<sub>3</sub> films, which exhibit the distinct formations of MA<sub>2</sub>SnI<sub>6</sub>, a yellow polymorph of FASnI<sub>3</sub>, and oxygen-combined black FASnI<sub>3</sub> after 12 h of aging.<sup>32</sup> The difference could be due to the fact that these samples were powders, which retarded the diffusion of O<sub>2</sub>/H<sub>2</sub>O into the bulk.

Conjugated molecules and polymers such as 2,2',7,7'-tetrakis(N,N-di-pmethoxyphenyl-amine)9,9'-spirobifluorene (spiro-OMeTAD) and poly(triarylamine) (PTAA) are often used as hole-transporting materials (HTMs) for perovskite solar cells. The highest occupied molecular orbital (HOMO) levels of these HTMs are between -5.1and -5.2 eV,<sup>23,24</sup> which fit the VBM of MAPbI<sub>3</sub> (-5.5 eV) and render efficient hole transfer by virtue of a sufficient offset energy (0.3-0.4 eV).<sup>12,27</sup> However, the VBMs of MASnI<sub>3</sub> and FASnI<sub>3</sub> are close to the typical HOMO levels of HTMs, suggesting the importance of developing a new HTM suitable for THPs. By adding the reported optical band gaps (1.26 eV for MASnI<sub>3</sub> and 1.40 eV for FASnI<sub>3</sub>)<sup>6,27</sup> to the VBMs, the conductionband minima (CBMs) were calculated to be -3.76 and -3.73 eV for MASnI<sub>3</sub> and FASnI<sub>3</sub>, respectively. These CBMs are moderate for efficient electron transfer to common electron-transporting materials (ETMs) including TiO<sub>2</sub>, perylene diimide, and fullerenes.<sup>36-38</sup>



**Figure 2-3.** (a) Powder XRD patterns of MASnI<sub>3</sub> and FASnI<sub>3</sub> with/without SnF<sub>2</sub>. The solid and dotted lines indicate fresh samples and 1-day-aged samples, respectively. Note that the XRD measurements were performed in the air and typically took 20 min for one scan. Therefore, fresh samples are not relevant to 0-min samples of PYS and TRMC. (b) Magnified (101) peaks at  $2\theta \approx 14.2^{\circ}$  for the fresh (top) and 1-day-aged (bottom) samples.

#### 2-2-2. Degradation of Optoelectronics of THPs

To examine the electronic degradation of THPs upon exposure to air,  $\phi\Sigma\mu$  transients (see eq. 1-5 in Chapter 1) were evaluated using TRMC (Figure 2-4a–d). As shown in Figure 2-4e, FASnI<sub>3</sub> + SnF<sub>2</sub> exhibits a progressive decrease of the  $\phi\Sigma\mu$  maximum ( $\phi\Sigma\mu_{max}$ ) on the minute scale.  $\phi\Sigma\mu_{max}$  of FASnI<sub>3</sub> is 5.3 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> without air exposure and



**Figure 2-4.** TRMC transients of (a) MASnI<sub>3</sub>, (b) MASnI<sub>3</sub> + SnF<sub>2</sub>, (c) FASnI<sub>3</sub>, and (d) FASnI<sub>3</sub> + SnF<sub>2</sub>. Colors indicate the total time of air exposure [from 0 min to 60 min]. (e)  $\phi\Sigma\mu_{max}$  of FASnI<sub>3</sub> (triangles) and FASnI<sub>3</sub> + SnF<sub>2</sub> (squares) plotted against air exposure time. Solid lines are double exponential fittings. (f)  $\phi\Sigma\mu_{max}$  values of MASnI<sub>3</sub> (triangles) and MASnI<sub>3</sub> + SnF<sub>2</sub> (squares) plotted against air exposure time. Solid lines represent triple-exponential fittings. (g) Normalized intensity of photoemission at 900 nm as a function of air exposure time. The inset shows the relative increase in the PL intensity by mixing SnF<sub>2</sub> into FASnI<sub>3</sub> or MASnI<sub>3</sub> after 1 min air exposure.

exponentially decreases to less than half that at 60 min.

The addition of SnF<sub>2</sub> to FASnI<sub>3</sub> results in an almost 2-fold enhancement in  $\phi \Sigma \mu_{max}$ ( $1.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), whereas the degradation is accelerated. This leads to a merging of the  $\phi \Sigma \mu_{max}$  values of FASnI<sub>3</sub> and FASnI<sub>3</sub> + SnF<sub>2</sub> into the same curve beyond 20 min. The enhancement of  $\phi \Sigma \mu_{max}$  by SnF<sub>2</sub> is relevant to the decrease of the dark carrier density<sup>4,9,39</sup> and the disappearance of the shoulder-shaped DOS in the PYS spectra. Therefore, the addition of SnF<sub>2</sub> is supposed to improve the initial electronic quality of FASnI<sub>3</sub> perovskite, but not to prevent the successive degradation caused by air exposure.

The  $\phi\Sigma\mu_{max}$  dependence of MASnI<sub>3</sub> on the air exposure time is somewhat strange in comparison with that of FASnI<sub>3</sub> (Figure 2-4f). The  $\phi\Sigma\mu_{max}$  values of MASnI<sub>3</sub> and MASnI<sub>3</sub> + SnF<sub>2</sub> at 0 min are 7.6 × 10<sup>-4</sup> and 2.7 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, which are slightly lower than that of FASnI<sub>3</sub>. Notably, they exhibit a rapid rise at 2–4 min by 35–150% and an exponential decrease afterward.

Photoemission provides an aspect of the electronic quality of THP. The time evolutions of the photoemission intensities of the THPs are shown in Figure 2-4g. Upon the addition of SnF<sub>2</sub>, the intensity at the initial time (~1 min) is considerably recovered (3.9-fold for FASnI<sub>3</sub> and 2.0-fold for MASnI<sub>3</sub>), in qualitative agreement with the effect of SnF<sub>2</sub> observed in PYS and TRMC. The decrease of the photoemission intensity is slightly faster for FASnI<sub>3</sub> + SnF<sub>2</sub> than for FASnI<sub>3</sub>. Conversely, the decrease for MASnI<sub>3</sub> is moderated by the addition of SnF<sub>2</sub>. These results are consistent with the minute-scale degradation found in the  $\phi\Sigma\mu_{max}$  of TRMC (Figure 2-4a–f). Note that the photoemission intensities themselves are higher for the SnF<sub>2</sub>-added MA(FA)SnI<sub>3</sub> samples than for the non-added ones even after air exposure, reiterating the improvement of the initial electronic quality of the THP upon SnF<sub>2</sub> addition. Because no distinct rise in photoemission is observed on the minute scale, the reason for the initial rise in TRMC cannot be inferred from the photoemission.

The decrease of  $\phi \Sigma \mu_{max}$  found in both air-exposed MASnI<sub>3</sub> and FASnI<sub>3</sub> is presumably due to the decomposition of 3-dimensional perovskite into SnI<sub>2</sub> or its H<sub>2</sub>O complex,<sup>32</sup> in analogy with the degradation mechanism of MAPbI<sub>3</sub>.<sup>1,40</sup> This degradation should cause only a decrease of  $\phi \Sigma \mu_{max}$ . Thus, another factor must be considered to explain the anomalous increase observed in  $\phi \Sigma \mu_{max}$  of MASnI<sub>3</sub>. The author hypothesize the formation of a low-dimensional perovskite MA<sub>2</sub>SnI<sub>6</sub> that is a pseudo-doubleperovskite of MA<sub>2</sub>Sn<sub>2</sub>I<sub>6</sub>, in which two Sn(II) ions are replaced with one oxidized form of Sn(IV). The VBM of MA<sub>2</sub>SnI<sub>6</sub> was found to be as deep as  $-6.35 \pm 0.05$  eV and remained almost constant up to 60 min of air exposure (Figure 2-5a). The PYS spectra underwent no deformation, indicating the good stability of MA<sub>2</sub>SnI<sub>6</sub>. TRMC evaluation reveals a  $\phi \Sigma \mu_{max}$  value of  $1.7 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 0 min and a mostly unchanged value of  $2.0 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> from 1 to 60 min (Figure 2-5b). These  $\phi \Sigma \mu_{max}$  are about twice those of FASnI<sub>3</sub> + SnF<sub>2</sub> and MASnI<sub>3</sub>, and the decay speed is greatly reduced. Therefore, MA<sub>2</sub>SnI<sub>6</sub> exhibits good optoelectronic properties, although it is still far inferior to the lead-based MAPbI<sub>3</sub>. A deep defect level in the band gap suggested by first-principles calculations is also noted.<sup>41</sup>

The XRD profile of MA<sub>2</sub>SnI<sub>6</sub> powder is shown in Figure 2-5c, together with those of the 1-day-aged MASnI<sub>3</sub> + SnF<sub>2</sub>. MA<sub>2</sub>SnI<sub>6</sub> sample indicates a pattern similar to that of the reconstructed Cs<sub>2</sub>SnI<sub>6</sub> with concurrent negative shifts due to the larger size of the MA cation compared to Cs. Notably, the aged MASnI<sub>3</sub> exhibits weak shoulders at  $2\theta = 12.8^{\circ}$ , 14.8°, 25.7°, and 29.8° attributed to the intense peaks of MA<sub>2</sub>SnI<sub>6</sub>. The appearance of the MA<sub>2</sub>SnI<sub>6</sub> peaks is more pronounced in the previously reported spin-coated MASnI<sub>3</sub> film



Figure 2-5. (a) PYS spectra of MA<sub>2</sub>SnI<sub>6</sub>. The corresponding air exposure time is appended in the figure. Solid black lines are linear fittings of a base and a rise to calculate an onset (= VBM). The inset shows the VBM dependence on the air exposure time. (b) TRMC transients of MA<sub>2</sub>SnI<sub>6</sub>. The inset shows  $\phi\Sigma\mu_{max}$  plotted against the air exposure time. (c) Powder XRD profiles of 1-day-aged MASnI<sub>3</sub> + SnF<sub>2</sub>, MA<sub>2</sub>SnI<sub>6</sub>, and Cs<sub>2</sub>SnI<sub>6</sub> reconstructed from the crystallographic data of ref 42. The right panel shows a magnification at  $2\theta = 13-16^{\circ}$ .
after 12 h of aging.<sup>32</sup> Accordingly, the formation of  $MA_2SnI_6$  in powder sample is evident from the XRD results.

With the results in mind, the rapid (2–4-min) increase in  $\phi \Sigma \mu_{max}$  found for MASnI<sub>3</sub> is assumed to be a result of the formation of MA<sub>2</sub>SnI<sub>6</sub>, in particular, on the surface of the powder. Unfortunately, the low-lying VBM and CBM are incompatible with common HTMs and ETMs. However, control of the formation of MA<sub>2</sub>SnI<sub>6</sub> might serve as an alternative approach for improving the stability of THPs. Notably, the inclusion of lowdimensional perovskite through the addition of phenylethylammonium (PEA) to FASnI<sub>3</sub> (+10% SnF<sub>2</sub>) was reported to afford a greatly enhanced stability and markedly improved PCE (5.94%)<sup>8</sup> in which the low-dimensional perovskite formed with PEA acts as the organic separating interlayer to block the inlet from oxygen and moisture. In the present study, addition of SnF<sub>2</sub> was found to improve the initial electronic quality (defect and photoconductivity maxima) of FASnI<sub>3</sub>, although the degradation was rather accelerated. The degradation is assumed to be caused by oxygen and moisture in analogy with that of MAPbI<sub>3</sub>,<sup>1,40,42</sup> and thus, the diffusion process of these reactants plays an important role,<sup>42</sup> which should be carefully examined for films with precisely controlled thicknesses, grain sizes, and compositions. The recent work on high-quality mixed-cation THP (8.12% PCE) is relevant to the further investigation of their degradation mechanism.<sup>43</sup>

# 2-2-3. Temperature-dependence of optical properties in LHP nanoparticles with methylammonium addition

Generally, the stability of LHPs in air is much higher than that of THPs because of the higher stability of Pb(II). However, the exposure to certain gas such as methylammonium ( $CH_3NH_2$ ) induce rapid and reversible transformation between LHP black film state and transparent state (Figure 2-6). Inspired by this behavior, the author



**Figure 2-6.** Pictures of MAPbI<sub>3</sub> thin films (a) before, (b) during, and (c) after  $CH_3NH_2$  gas exposure.  $CH_3NH_2$  gas was extracted from  $CH_3NH_2$  solution dissolved in methanol (40 wt%).

investigated the interaction between LHP nanoparticles and CH<sub>3</sub>NH<sub>2</sub>.

The MAPbBr<sub>3</sub> NPs were synthesized using the ligand-assisted reprecipitation method.<sup>44</sup> In this way, NPs were readily formed even in air by dropping a dimethylformamide (DMF) solution of CH<sub>3</sub>NH<sub>3</sub>Br:PbBr<sub>2</sub>:*n*-octylamine:oleic acid (1:1.25:0.75:9.9 by molar fraction) into vigorously stirred toluene (Figure 2-7a). The n-octylamine acts as a capping agent for the NPs, while the oleic acid prevents their



**Figure 2-7.** (a) Illustration of preparation procedure for MAPbBr<sub>3</sub> NP (left) and subsequent LCST system of NP+CH<sub>3</sub>NH<sub>2</sub> (right). (b) Examination on the roles of involved chemicals (CH<sub>3</sub>NH<sub>2</sub>, oleic acid, and methanol). The upper panel shows the sequential addition of a methanol solution of CH<sub>3</sub>NH<sub>2</sub> and oleic acid, which leads to LCST behavior. Meanwhile, addition of methanol, oleic acid, or methanol and oleic acid did not cause any changes, indicating that CH<sub>3</sub>NH<sub>2</sub> plays a key role in the observed phenomena. This demonstrates that oleic acid fragmentizes the intermediate co-crystal into soluble PbBr<sub>2</sub> wire and prevents excessive NP growth. The white object at the bottom of the vial is a stirring bar.

excessive growth.<sup>44</sup> This NP suspension was subsequently added dropwise into 2 mL of toluene in the presence of a small amount of methylamine (10 µL of 40 wt% CH<sub>3</sub>NH<sub>2</sub> in methanol), which caused the yellowish NP suspensions to immediately decompose and create a transparent solution. The addition of methanol and/or oleic acid without CH<sub>3</sub>NH<sub>2</sub> did not cause any change in the NP suspension, thus confirming the need for CH<sub>3</sub>NH<sub>2</sub> to decompose the NPs (Figure 2-7b). This idea came from the observation that a dark brown MAPbI<sub>3</sub> film is quickly and reversibly changed to a translucent film by exposing it to CH<sub>3</sub>NH<sub>2</sub> vapor (Figure 2-6). The author has since examined other vapors such as NH<sub>3</sub>, dimetylamine, n-propylamine, n-octylamine, DMSO (dimethyl sulfoxide), DMF, acetone, methanol, and ethanol, but of these, a clear reversible change is only found with NH<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub>. The use of NH<sub>3</sub> vapor induces a transition to a white film,<sup>45</sup> but excessive exposure results in an irreversible change, i.e., it only returned to perovskite when the film was thermally annealed at  $\approx 110$  °C. Using a methanol solution of NH<sub>3</sub> in place of CH<sub>3</sub>NH<sub>2</sub> also produced decomposition of the NPs, but the suspension of white crystals remained insoluble. Similarly, although efficient and complete dissolution of the white crystals was possible with n-propylamine, no change was observed upon heating to 80 °C. Based on this, CH<sub>3</sub>NH<sub>2</sub> was considered to be the most appropriate agent for creating a thermoresponsive function at moderate temperature, which may be associated with its ability to heal defects in collapsed MAPbI<sub>3</sub> crystals.<sup>46</sup> The versatile nature of CH<sub>3</sub>NH<sub>2</sub> is also evident from the transformation of 2D HPbI3 to 3D MAPbI3 perovskite upon exposure to CH<sub>3</sub>NH<sub>2</sub> gas, which delivers a high-quality LHP film and efficient solar cell.<sup>13</sup> The unique LCST behavior is also linked to the inverse solubility of MAPbI<sub>3</sub> in  $\gamma$ butyrolactone.47,48

As shown in Figure 2-8a, increasing the solution temperature from 20 to 60 °C causes the photoabsorption tail at 600–900 nm to continuously raise due to light scattering by the NPs formed, which is accompanied by the evolution of the excitonic peak of MAPbBr3 at  $\approx$ 525 nm.<sup>49</sup> On heating, the transparent solution turned yellowish, which was accompanied by a drastic shift in photoemission from blue (430 nm) to green (525 nm) (Figure 2-8b). Remarkably, the decomposition and formation of MAPbBr<sub>3</sub> NPs is fully reversible as long as CH<sub>3</sub>NH<sub>2</sub> remains in solution (five cycles were tested, Figure 2-8c), but the transition speed of around 10–20 s is limited by the heat exchange between the solution and heat source.

Figure 2-9a represents the temperature dependence of photoabsorption at 700 and 800 nm, in which a sigmoidal increase in light scattering intensity can be observed that follows a similar trend to the LCST transition of PNIPA.<sup>14–16</sup> This is in sharp contrast to the MAPbBr<sub>3</sub> NPs without CH<sub>3</sub>NH<sub>2</sub>, which exhibit a flat dependence on temperature.



**Figure 2-8.** (a) photoabsorption and (b) photoemission ( $\lambda_{ex} = 350 \text{ nm}$ ) of NP+CH<sub>3</sub>NH<sub>2</sub> solution on heating from 20 °C to 60 °C. The gray lines are the intermediate temperatures (white at low temperature to dark at high temperature). The insets show photographs of solution at 20 °C (lower) and suspension at 60 °C (upper) with (a) room lighting and (b) exposure to a CW laser ( $\lambda_{ex} = 375 \text{ nm}$ ) in darkness. (c) Plots of intensities at ~ 525 nm (green) and ~430 nm (blue) with the sequential number (even numbers divided by two represent the numbers of cycle).

Importantly, the  $T_c$  is determined by the concentration of CH<sub>3</sub>NH<sub>2</sub> and oleic acid, i.e., NP+CH<sub>3</sub>NH<sub>2</sub> (A) has a  $T_c$  of  $\approx$ 40 °C that is increased to  $\approx$ 50 °C with 3.7-fold increase in CH<sub>3</sub>NH<sub>2</sub> and 1.5-fold increase in oleic acid in NP+CH<sub>3</sub>NH<sub>2</sub> (B) (solid and open circles in Figure 2-9a, respectively). Note that an increase in either CH<sub>3</sub>NH<sub>2</sub> or oleic acid can shift the sigmoidal curve to a higher temperature, but this deforms the curve in a different way (Figure 2-9b, c). Specifically, an increase in oleic acid simply produces a sharper transition at higher  $T_c$ , whereas CH<sub>3</sub>NH<sub>2</sub> leads to the appearance of two distinct stepwise transitions at  $\approx$ 40 and  $\approx$ 55 °C. This suggests that each compound plays a different role in the multiple phase transition behind the LCST phenomenon.

Changing the relative molar concentration of PbBr<sub>2</sub> was used to create an LCSTtype phase diagram (Figure 2-9d), the minimum point of which is at  $\approx$ 55 °C. Phase transition is more manifest in the photoemissions presented in Figure 2-9e, wherein blue emission at 430 nm decreases with temperature and a green emission at 525 nm simultaneously emerges. These emissions crossover in terms of intensity in the early stage of phase transition, because the small MAPbBr<sub>3</sub> NPs that were initially formed are highly green emissive. Due to the same reason, the onset temperature of 525 nm emission intensity ( $\approx$ 35 °C) is slightly lower than the  $T_c$  observed in the photoabsorption ( $\approx$ 40 °C). During the formation and growth of NPs between 40 and 45 °C, a red-shift of  $\approx$ 10 nm is observed along with an increase in intensity that can be ascribed to the quantum size effect<sup>50</sup> (Figures 2-9f). Even after the complete formation of NPs (>48 °C), a small redshift of 3–5 nm still occurs in both the absorption and photoemission peaks, which in turn reduces the photoemission intensity. This can be linked to the formation of nonradiative charge trapping sites in NPs, which are regarded as the cause of photocurrent loss in MAPbI<sub>3</sub> solar cells.<sup>51,52</sup> Electron–phonon coupling that reduces the optical bandgap of semiconductor could also be a possible mechanism for the red-shift, which has been



**Figure 2-9.** LCST transition on heating and phase diagram of MAPbBr<sub>3</sub> NP + CH<sub>3</sub>NH<sub>2</sub>. (a) Change in photoabsorption of LCST system A (closed circles at 800 nm) and B (open circles at 700 nm). Black solid and dotted lines are least-mean-square fits of three-state model (see the text). Open squares are control experiments of MAPbBr<sub>3</sub> NP with methanol and without CH<sub>3</sub>NH<sub>2</sub> (the fitting line is linear fit). Photoabsorption change with increased (b) CH<sub>3</sub>NH<sub>2</sub> concentration by 1.5-fold and (c) oleic acid concentration by 1.5-fold. (d) Phase diagram of NP+CH<sub>3</sub>NH<sub>2</sub>. Solid line is an eyeguide and OA is oleic acid. (e) Evolution of photoemission intensity at 525 nm (circles) and 430 nm (triangles) of NP+CH<sub>3</sub>NH<sub>2</sub> (A). The open squares are control experiments of NP without CH<sub>3</sub>NH<sub>2</sub> ( $\lambda_{ex} = 350$  nm). (f) Spectral shift in photoemission peak (closed circles) and absorption peak (open circles) of NP+CH<sub>3</sub>NH<sub>2</sub>. The inset shows photoemission spectral change with increasing temperature from 40 °C to 60 °C. Solid lines are eye-guides. Gray areas in panels (e) and (f) correspond to regions of interest due to their large shift in photoemission.

observed in temperature- and pH-dependent aggregation-induced emission of 2D perovskite  $[(C_nH_{2n+1}NH_3)_2PbI_4]^{.53}$ 

### 2-2-4. The mechanism of LCST behavior of LHPs nanoparticles

To provide structural and mechanistic insight into the LCST behavior observed, the MAPbBr<sub>3</sub> NPs and their complex with amines were subjected to X-ray diffraction (XRD) analysis. A spin-coated film of MAPbBr<sub>3</sub> NPs on quartz was found to produce an indices-assigned XRD spectrum identical to that presented in a previous report<sup>54</sup> (Figure 2-10a). However, a dropcasted film of transparent NP+CH<sub>3</sub>NH<sub>2</sub> solution had the same spectrum as the original MAPbBr<sub>3</sub> NPs, because the CH<sub>3</sub>NH<sub>2</sub> immediately evaporated.



**Figure 2-10.** XRD results and LCST mechanism. (a) XRD spectra ( $\lambda = 1.54$  Å) of MAPbBr<sub>3</sub> NP film, NP film treated with NH<sub>3</sub> vapor, and NP+NH<sub>3</sub> reconstructed from single-crystal XRD. (b) Crystal structure of NH<sub>3</sub>·PbBr<sub>2</sub>·DMF determined by single crystal XRD ( $\lambda = 0.71$  Å). (c) Magnified view of (b), wherein the coordination of NH<sub>3</sub>···Pb is connected by a dotted line. A pair of cofaced PbBr<sub>2</sub> networks is represented by a rhombic area. Pb and two Br atoms of cofaced PbBr<sub>2</sub> network are connected to form a polygon. (d) (1 1 –1) and (0 2 0) planes of NH<sub>3</sub>·PbBr<sub>2</sub>·DMF crystal determined by using single crystal XRD. (e) Normalized photoemission spectra of solution state of NP + CH<sub>3</sub>NH<sub>2</sub> at 20 °C (red,  $\lambda ex = 350$  nm) and NH<sub>3</sub>·PbBr<sub>2</sub>·DMF co-crystal (blue,  $\lambda_{ex} = 290$  nm).

The MAPbBr<sub>3</sub> NP film was therefore exposed to NH<sub>3</sub> vapor, which cocrystalizes more strongly than CH<sub>3</sub>NH<sub>2</sub>, and this produced white crystals stable enough for XRD measurement. This combination of NP+NH<sub>3</sub> produced a complete change in the spectral features, with the most intense peak at a 20 of 14.9° for MAPbBr<sub>3</sub> being moved to 8.4°. The spectrum contains weakened peaks of the original NP [e.g., (0 0 1), (0 1 1), (0 0 2), ...] and unassigned complex pattern, in particular, at  $2\theta = 12.0^{\circ}-13.4^{\circ}$  and  $25.4^{\circ}-26.5^{\circ}$ , the latter of which could be due to NP+NH<sub>3</sub> complex and regenerated PbBr<sub>2</sub>.

By keeping a DMF solution of NP+NH<sub>3</sub> in a toluene-saturated vial under ambient conditions for one day, needle-shaped single crystals were successfully obtained (see Experimental). Analysis of these single crystals revealed a novel structure of NH<sub>3</sub>·PbBr<sub>2</sub>·DMF cocrystals, which included a 1D PbBr<sub>2</sub> network with a Pb–Br distance of 2.97–3.03 Å (Figure 2-10b). In addition, a pair of PbBr<sub>2</sub> wires was cofaced with



**Figure 2-11.** Examination of LCST behaviors of CH<sub>3</sub>NH<sub>3</sub>Br (MABr) and PbBr<sub>2</sub>. (a) MABr in DMF was dispersed into toluene and then (CH<sub>3</sub>NH<sub>2</sub> in methanol oleic acid, n-octylamine), (CH<sub>3</sub>NH<sub>2</sub> in methanol, oleic acid), or (n-octylamine) was added. All of them led to dissolution, but did not show any LCST behaviors. (b) PbBr<sub>2</sub> in DMF was dispersed into toluene and then CH<sub>3</sub>NH<sub>2</sub> in methanol and oleic acid were added, which led to dissolution. Upon heating, a white suspension is generated. These examinations support that the PbBr<sub>2</sub> is responsible for the formation of co-crystal and LCST behavior. In addition, MABr is dissolved when the PbBr<sub>2</sub> co-crystal is formed, but is trapped into MAPbBr<sub>3</sub> NP at a high temperature. The white object at the bottom of the vial is a stirring bar.

slipping along the longitudinal a-axis, and NH<sub>3</sub> coordinates with Pb ions at a distance of 2.40 Å (Figure 2-10c). The isotropic XRD spectrum reconstructed from the single crystal XRD data is analogous to that of a MAPbBr<sub>3</sub> NP film treated by NH<sub>3</sub> vapor (Figure 2-10a). The most intense peak of the reconstructed spectrum at the low angle is composed of two peaks  $[2\theta = 8.9^{\circ} \text{ and } 9.1^{\circ}, \text{ assigned to } (1 \ 1 \ -1) \text{ and } (0 \ 2 \ 0), \text{ respectively}];$  however, it is likely merged into one peak in the NP+NH<sub>3</sub> film. Anisotropic orientation in the film may be a reason, because  $(1 \ 1 \ -1)$  and  $(0 \ 2 \ 0)$  planes are perpendicular to each other (Figure 2-10d). Most importantly, the NH<sub>3</sub>·PbBr<sub>2</sub>·DMF cocrystal produces a blue emission that peaks at 415 nm (Figure 2-10e), which is almost identical to that observed in the solution phase of NP+CH<sub>3</sub>NH<sub>2</sub> (peaks at 409 and 433 nm). The blue emission from the LCST system is therefore ascribed to a 1D PbBr<sub>2</sub> network. The excess bromine anion (Br<sup>-</sup>) and methylammonium cation (MA, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) are dissolved in the solution by the aid of oleic acid and n-octylamine, as confirmed from stepwise addition of these reagents and no LCST behavior without PbBr<sub>2</sub> (Figure 2-11a). The PbBr<sub>2</sub> solution without MABr generates the cocrystals at a high temperature but no MAPbBr<sub>3</sub> NP (Figure 2-11b). These results are consistent with the lack of MABr in the composition of the cocrystal. The analogous complex adducts of MAI·PbI2·xDMSO in solid state also supports the obtained crystallographic results.55-57

In light of the XRD and optical spectroscopy results, the mechanism behind the LCST behavior was suggested to be that illustrated in Figure 2-12. Although the NP+CH<sub>3</sub>NH<sub>2</sub> solution was unable to produce stable single crystals, most likely due to the weak coordination of CH<sub>3</sub>NH<sub>2</sub> with Pb and distance between paired PbBr<sub>2</sub> wires, it is believed that a similar intermediate crystal is involved. The phase transition in Figure 2-9a consists of two sigmoidal curves: a small, gentle transition from room temperature to  $T_c$ ; and a dominant, steep transition above  $T_c$ . Accordingly, the curve was analyzed using a three-state model given by the linear combination of two sigmoidal (Boltzmann) functions<sup>57</sup>

Abs = 
$$\sum_{n=1}^{2} \frac{A_n}{1 + \exp(-\frac{T - T_n}{\varepsilon_n})} + A_0$$
 (2-1)

where  $A_n$  (n = 0, 1, 2) is a scaling factor or baseline,  $T_n$  (n = 1, 2) is the transition temperature, and  $\varepsilon_n$  (n = 1, 2) is the degree of transition sharpness with temperature. A least-mean-square fitting showed good agreement with the experimental curves (the black solid and dotted lines in Figure 2-9a). Indeed, the three-state model is consistent with the emergence of intermediate white suspensions at the 2nd state (inset picture of Figure 2-12-ii), which are notably different to the yellowish MAPbBr<sub>3</sub> NP suspension formed at the 3rd state (Figure 2-12-iii). The solution state below the  $T_c$  is assumed to be a 1D wire



**Figure 2-12.** Mechanistic illustration of LCST behavior based on three-state model: (i) solution state, (ii) intermediate cocrystal state, and (iii) MAPbBr<sub>3</sub> NP state. The insets of each state are photographs under room light with exposure to a 375 nm CW laser.

of PbBr<sub>2</sub> coordinated by CH<sub>3</sub>NH<sub>2</sub> and oleic acid (1st state, Figure 2-12-i). Without oleic acid, the suspension of white cocrystals formed via CH<sub>3</sub>NH<sub>2</sub> coordination to Pb did not disappear, thereby underscoring the key role oleic acid plays in fragmentizing the intermediate cocrystal into soluble PbBr<sub>2</sub> wire and preventing excessive NP growth. The presence of oleic acid without CH<sub>3</sub>NH<sub>2</sub>, of course, causes no change in the NPs, highlighting the need for both CH<sub>3</sub>NH<sub>2</sub> and oleic acid to create LCST behavior (Figure 2-7b).

Dynamic light scattering (DLS) confirmed that the NP+CH<sub>2</sub>NH<sub>2</sub> solution has a relatively stable distribution at 30–50 °C (below  $T_c$ ) and a small  $D_{50\%}$  of 2.4–3.5 nm, as shown in Figure 2-13a. This size corresponds to 6–8 units of the PbBr<sub>2</sub> network, as illustrated in Figure 2-12-i. At 61 °C (above  $T_c$ ), an abrupt and significant increase in particle size (~2.0 µm) was observed that corresponds to the formation of a NP suspension and aggregation. Note that the particle distribution evaluated by DLS is sensitive to the presence of larger particles, because the scattering intensity is dominated by the volume of particles. Cooling from 61 to 18 °C decomposed the NPs, and so the  $D_{50\%}$  was reduced again to ~2.5 nm.

Picosecond fluorescence lifetime spectroscopy revealed two or three decay components in the photoemission of the LCST system (Figure 2-13b). In contrast, the emission of normal MAPbBr<sub>3</sub> NPs at 525 nm mostly exhibited a single exponential decay (average lifetime  $\tau_{ave} = 7.2$  ns at 25 °C, Figure 11c). Meanwhile, the  $\tau_{ave}$  of the LCST system at 430 nm did not undergo any discernible change upon heating (~1.2 ns for 20–60 °C), but those at 525 nm were marginally elongated from 13.2 to 16.7 ns (Figure 2-13c). It was noticed that the lifetime is affected by the rate at which the temperature is increased and the concentration of the chemicals involved. A short lifetime is caused by

trapping sites<sup>58</sup> that are generated during the aggregation of NPs and/or an irregular transition from the intermediate co-crystal. Notably, diluting the solution and rapid heating produced photoemission quantum yields (QY) as high as 85% with an extended  $\tau_{ave}$  of 73.7 ns (LCST2 in Figure 2-13b). This QY is equal to that previously reported for MAPbBr<sub>3</sub> NPs (80–90%),<sup>59-61</sup> and much larger than that for the LCST system without any optimization (typically a few percent).

Though first developed in perovskite NPs, further evolution of this molecular/ionic LCST system is foreseen owing to its versatile function of providing not only a transition between a solution and suspension, but also a drastic change in optical properties. For instance, both convection of fluid and temperature change are simultaneously visualized as fluorescent traces under UV light. Figure 2-14a shows a snapshot of the MAPbBr<sub>3</sub>-based LCST solution during heating on a hot plate, where polystyrene is dissolved to increase the viscosity of the solution. The low viscous solution indicates a rapid and relatively homogeneous convection, whereas the high viscous solution shows a slow



**Figure 2-13.** DLS and ps fluorescence lifetime spectroscopy of MAPbBr<sub>3</sub> NP+CH<sub>3</sub>NH<sub>2</sub>. (a) Particle size distribution of NP+CH<sub>3</sub>NH<sub>2</sub> on heating from 30–50 °C (below  $T_c$ ) to 61 °C (above  $T_c$ ), and cooling to 18 °C. (b) Normalized photoemission decays at 525 nm for MAPbBr<sub>3</sub> NP (25 °C, orange), LCST1 (NP+CH<sub>3</sub>NH<sub>2</sub> at 60 °C, green), and LCST2 with high quantum efficiency (NP+CH<sub>3</sub>NH<sub>2</sub> at 65 °C, violet).  $\lambda_{ex}$  = 377 nm. The black lines are multiexponential fittings. (c) Average lifetimes of 525 nm decays of NP, LCST1, and LCST2.

diffusion followed by a sudden inhomogeneous build up, which forms Aurora-like traces. The latent green-emissive traces remain as long as the temperature is above  $T_c$ . Upon cooling on a cold plate, the bright photoluminescence disappears from the bottom and the solution turns back to the blue emission state (Figure 2-14b).



On a hot plate

On a cold plate

**Figure 2-14.** Visualization of fluid convection and temperature change in a toluene solution of polystyrene and MAPbBr<sub>3</sub>+CH<sub>3</sub>CH<sub>2</sub> under 365 nm irradiation. (a) Upon heating on a hot plate. (b) Upon cooling on a cold plate.

### 2-3. Conclusion

In this chapter, the investigation of the transformation behavior of THPs and LHPs with molecular adsorption were described. With the presence of oxygen, THPs showed significant deepening of VBM level in PYS evaluation. It was revealed that the addition of SnF<sub>2</sub> does not impact the VBMs without air exposure  $(-5.02 \pm 0.03 \text{ eV} \text{ for MASnI}_3)$ and  $-5.13 \pm 0.03$  eV for FASnI<sub>3</sub>), but suppress the defect-related DOS near the onset (deeper than -4.7 eV). The VBMs were gradually shifted to the deeper side after a few minutes of air exposure. This was accompanied by the deterioration of the PYS profiles, but was partly moderated by mixing with SnF<sub>2</sub>. TRMC transient maxima of FASnI<sub>3</sub> progressively decreased with air exposure, where the addition of SnF<sub>2</sub> was found to improve the initial electronic quality instead of retarding the degradation itself. MASnI<sub>3</sub> exhibited the same degradation behavior, but concomitant with the anomalous peak at 2-4 min. The reason for the peak was suggested to be the formation of MA<sub>2</sub>SnI<sub>6</sub>, which shows a higher TRMC signal, deeper VBM ( $-6.35 \pm 0.05$  eV), and better stability. The author foresees further paths to an efficient, stable lead-free perovskite solar cell, where the energetics and degradation behavior revealed in the present study could be of help in designing the device structure and processing.

Meanwhile, LHPs did not show such a rapid changing with air exposure, but showed rapid and reversible transformation with CH<sub>3</sub>NH<sub>2</sub> gas exposure. Inspired by the quick response to CH<sub>3</sub>NH<sub>2</sub> vapor, the author developed a LCST system based on molecular/ionic materials that provides unique photoemission switching with a QY of up to 85%, as well as a transition between a solution and suspension. From single-crystal XRD analyses, a 1-dimensional PbBr<sub>2</sub> network coordinated by amine was identified as the blue-emitting entity. Furthermore, this intermediate phase was found to play an important role in generating green-emitting MAPbBr<sub>3</sub> NPs at high temperature. Accordingly, a three-state model was suggested to account for the observed transition in photoabsorption, wherein oleic acid and CH<sub>3</sub>NH<sub>2</sub> mediate a reversible self-organization in the transition from a solution (1<sup>st</sup> state) to an intermediate suspension (2<sup>nd</sup> state) and NP suspension (3<sup>rd</sup> state). Given the ease with which the cloud point and emission color can be tuned via compositional engineering of concentration and halogen exchange, it is anticipated that this LCST system based on an organic-inorganic perovskite scaffold will give rise to a diverse range of new applications in thermoresponsive photonic materials.

# 2-4. Experimental

# 2-4-1. Preparation and evaluation of THPs powder

### Sample preparation

MAI and FAI were purchased from Tokyo Chemical Industry (TCI) Co. Ltd. SnF<sub>2</sub> was purchased from Sigma-Aldrich Co. Llc. These materials were used as received. Dehydrated ethanol (super dehydrated) and N,N-dimethylformamide (DMF, dehydratedsuper) were purchased from Wako Pure Chemical Industries Ltd. and Kanto Chemical. Co. Inc., respectively, which were further dried over molecular sieves and degassed by Ar gas bubbling for 1h before use. As a purified precursor for THPs,  $[SnI_2(dmf)]$  complex was prepared by recrystallization from a DMF solution of SnI<sub>2</sub> (sublimed, TCI) in an Arfilled glove box ( $O_2 \sim 10$  ppm). The details on preparation and characterization of the [SnI<sub>2</sub>(dmf)] complex will be reported elsewhere.<sup>23</sup> In an Ar-filled glove box, MAI (or FAI), [SnI<sub>2</sub>(dmf)], and SnF<sub>2</sub> in DMF (1 M) were dissolved in ethanol at the stoichiometric ratio (1:1:0 or 1:1:0.2 in molar fraction). The reaction mixture was stirred at 80 °C for 30 min. The obtained pale green solution was cooled down to afford blackish green crystalline powder. After filtration and washed with ethanol, powder of MASnI<sub>3</sub> or FASnI<sub>3</sub> with/without SnF<sub>2</sub> was obtained. MA<sub>2</sub>SnI<sub>6</sub> was prepared in the same fashion using MAI and a SnI<sub>4</sub> precursor (purchased from Aldrich) at 2:1 stoichiometry (no addition of SnF<sub>2</sub>).

# Photoelectron yield spectroscopy

PYS experiments were carried out using a Bunko Keiki BIP-KV201 (accuracy:  $\pm 0.02 \text{ eV}$ , extraction voltage = 10 V) in a vacuum ( $<10^{-2}$  Pa). In a N<sub>2</sub>-filled glove box (O<sub>2</sub> ~ 0.0 ppm), powder samples were placed on a conductive carbon tape on glass, which was contacted through aluminum tape and an Au-coated electrode. Note that carbon tape without samples gives a deep onset energy (~ -6.9 eV), and the intensity of the photoelectron yield is about two orders of magnitude smaller than those of THPs. Thus, the effect of the carbon tape is negligible. The sample was transferred in a pass box from the glove box to another one (O<sub>2</sub> ~ 50 ppm) that was directly connected to the chamber of the PYS. After each measurement (about 20 min in total), the sample was moved outside the glove box to be exposed to air. The air exposure time is the integrated value of each exposure time. The temperature and humidity of the air are ~ 25°C and 60%, respectively, which were not precisely controlled, but mostly constant.

### Time-resolved microwave conductivity and photoemission spectroscopy

In a N<sub>2</sub>-filled glove box, powder samples were placed on adhesive tape on a quartz plate and set in a sealed resonant cavity. The sample in a cavity was moved outside, set in a microwave circuit, and subject to a TRMC evaluation using continuous microwaves at approximately 9.1 GHz. The third harmonic generation of a Nd:YAG laser (Continuum Inc., Surelite II, 5–8-ns pulse duration, 10 Hz) was used as the excitation (incident photon density,  $I_0 = 1.8 \times 10^{15}$  photons cm<sup>-2</sup> pulse<sup>-1</sup>). The photoconductivity transient  $\Delta \sigma$  was converted to  $\phi \Sigma \mu$  based on the eq. 1-5 in Chapter 1.

After the first measurement (=0 min), the cavity was open to air (~ 25°C and 60% humidity), and measurements were conducted (the air exposure time is the time after opening the cavity). Photoemission spectroscopy was performed using a Jasco FP-8300 spectrometer. A powder sample on a quartz plate was prepared in the same way as those of the TRMC evaluation. The time evolution of emission ( $\lambda_{ex} = 500$  nm,  $\lambda_{em} = 900$  nm) was recorded from 1 min after the removal of a sample from a glove box. Powder X-ray diffraction (XRD) data were collected on a Rigaku MiniFlex-600 using Cu–K<sub>a</sub> radiation ( $\lambda = 1.54187$  Å) at room temperature in the air.

#### 2-4-2. Preparation and evaluation of LHPs nanoparticles (NPs)

### Preparation of NPs and LCST Solution.

The 0.08 mmol CH<sub>3</sub>NH<sub>3</sub>Br, 0.10 mmol PbBr<sub>2</sub>, 10  $\mu$ L *n*-octylamine, and 250  $\mu$ L oleic acid were dissolved in 5 mL of DMF. To prepare MAPbBr<sub>3</sub> NP+CH<sub>3</sub>NH<sub>2</sub> (A), 80  $\mu$ L of the abovementioned DMF precursor solution was added dropwise into 2.5 mL of vigorously-stirred dehydrated toluene to produce a suspension of MAPbBr<sub>3</sub> NPs. A 0.5 ml sample of this solution was then added to 2 mL of dehydrated toluene containing 10  $\mu$ L of a 40% CH<sub>3</sub>NH<sub>2</sub> (ca. 9.8 mmol mL<sup>-1</sup>) methanol solution and 2  $\mu$ L of oleic acid, which produced a transparent solution. For MAPbBr<sub>3</sub> NP+CH<sub>3</sub>NH<sub>2</sub> (B), 80  $\mu$ L of the DMF precursor solution was then added to 2 mL of toluene to create a NP suspension. A 0.5 mL sample of this NP suspension was then added to 2 mL of oleic acid diluted ten-fold in toluene. A high fluorescence quantum yield (HQY) solution was obtained through ten-fold dilution of (A) by adding 60  $\mu$ L of the DMF precursor solution and 10  $\mu$ L of oleic acid diluted ten-fold in toluene.

### General Measurement

UV-vis and fluorescence spectroscopy were performed using a Jasco V-730 UV-Vis spectrophotometer and Jasco FP-8300 spectrometer, respectively. The fluorescence quantum yield was evaluated relative to a fluorescein reference (QY = 92%) using these same spectrometers after their sensitivity was calibrated with Rhodamine B. Picosecond fluorescence lifetime measurements based on the time-correlated single-photon counting (TCSPC) technique were performed using a HORIBA model FluoroCube 3000U-UltraFast-SP spectrophotometer ( $\lambda_{ex} = 377$  nm). Dynamic light scattering measurements were performed using a MicrotracBEL model NanotracWave UT-151 ( $\lambda_{probe} = 780$  nm, detectable range: 0.8 nm ~ 6.5 µm) after passing each solution through a 0.45 µm membrane filter. Powder X-ray diffraction data were collected on a Rigaku RINT-2000 using graphite-monochromatised Cu–K<sub>a</sub> radiation ( $\lambda = 1.54187$  Å) at room temperature.

### Single crystal XRD

Needle-shaped single crystals were obtained by poor solvent (toluene) diffusion of a DMF solution of NPs and NH<sub>3</sub> (Figure 2-15). Diffraction data were collected using a Rigaku XtaLAB mini with Mo–K $\alpha$  radiation ( $\lambda$ = 0.71075 Å) at -60 °C. For C<sub>3</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>OPb,  $M_w$  = 457.13, a = 4.239(4), b = 19.47(2), c = 11.757(13) Å,  $\alpha = 90^\circ$ ,  $\beta = 99.515(9)^\circ$ ,  $\gamma = 90^\circ$ , V = 957.1(18) Å<sup>3</sup>, T = 213 K, monoclinic, space group  $P2_1/n$  (#14), Z = 4,  $\rho_{calcd} = 3.172$  g cm<sup>-3</sup>.



**Figure 2-15.** Needle-shaped single crystals of NH<sub>3</sub>-PbBr<sub>2</sub>-DMF grown by solvent diffusion method.

# 2-5. Reference

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# **Chapter 3: Development of Solution Processed Pb-free Chalcogenide Thin Film for Optoelectronic Application**

# **3-1. Introduction**

Metal chalcogenides with two-dimensional (2D) atomic layers are an emerging class of materials with rich optical and electronic properties.<sup>1–3</sup> Transition metal dichalcogenides such as WS<sub>2</sub>, MoS<sub>2</sub>, and MoSe<sub>2</sub> exhibit large charge carrier mobilities above 50 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in ambipolar field effect transistors (FETs)<sup>4,5</sup> and subthermionic tunneling behavior in FETs.<sup>6</sup> Besides, bismuth sulfide (Bi<sub>2</sub>S<sub>3</sub>) is potentially suitable for optoelectronic applications, owing to its significantly large Hall mobility (257 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, a thermally-evaporated *n*-doped film)<sup>7</sup> and moderate bandgap of 1.3–1.6 eV<sup>8,9</sup> (dependent on the grain size and stoichiometry).<sup>10</sup>

Although there are several reports on Bi<sub>2</sub>S<sub>3</sub>-based photovoltaic cells<sup>8,10,11–14</sup> and photodetectors,<sup>15,16</sup> their widespread use and improved performance are limited by current film processing techniques, which require a trade-off between electronic and morphological qualities. As described in chapter 1, deposition using a colloidal nanoparticles (NPs)<sup>8,10,11,12</sup> suspension, chemical bath deposition (CBD),<sup>17,18</sup> successive-ionic-layer-adsorption-reaction (SILAR),<sup>19,20</sup> and spray pyrolysis (SP)<sup>21,22</sup> allow for the fabrication of smooth films over large areas, however the electronic properties are degraded by the small grain size and presence of impurities. By contrast, thermal decomposition of bismuth triethyldithiocarbonate (Bi(EtXa)<sub>3</sub>) results in a highly-crystalline film,<sup>23,24</sup> though the film displays a mesoporous or nanorod morphology detrimental to long-range carrier transport. So far, a solution process that mitigates this trade-off has not yet been realized. Thermal evaporation yields a smooth but sulfur-poor film, giving a metallic bismuth or highly electron-doped Bi<sub>2</sub>S<sub>3</sub> film (10<sup>19</sup> cm<sup>-3</sup>)<sup>7</sup> that can only be used as a negative electrode buffer.<sup>14</sup>

In this chapter, the effectiveness of a two-step technique for the facile fabrication of a Bi<sub>2</sub>S<sub>3</sub> film involving spin-coating of a propionic acid (PA, CH<sub>3</sub>CH<sub>2</sub>COOH) solution of bismuth acetate (Bi(OAc)<sub>3</sub>, OAc = CH<sub>3</sub>COO<sup>-</sup>) and thiourea (CS(NH<sub>2</sub>)<sub>2</sub>), followed by film crystallization under diluted H<sub>2</sub>S gas is described. This sequential process was proposed to reconcile the current trade-off issue by separating the nucleation and growth steps. Hereafter, this process is referred to as a chemically-assisted spin-coat and crystallization (CASC) process. The morphology, optoelectronics, and other characteristics of a photoresistor device utilizing a CASC film were investigated and compared to those of similar devices prepared by conventional methods.

# **3-2.** Results and Discussion

# **3-2-1.** Development of chemically-assisted spin-coat and crystallization (CASC) process

A schematic of the CASC process is illustrated in Figure 3-1a. A mixture of  $Bi(OAc)_3$  and thiourea in PA was found to be the most suitable precursor solution for the  $Bi_2S_3$  CASC process, after performing rigorous combinatorial surveys of different solvents [*N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene, alcohol, carboxylic acid, and PA], bismuth sources [Bi(OAc)\_3, Bi(EtXa)\_3, bismuth nitric acid (Bi(NO\_3)\_3), BiCl\_3, and BiI\_3], and sulfur sources [thiourea and thiomalic acid]. Upon pre-thermal annealing of a spin-coated film at 150 °C for 50 s, thiourea is decomposed to gaseous CS<sub>2</sub>, H<sub>2</sub>NCN, NH<sub>3</sub>, HNCS, and H<sub>2</sub>S,<sup>25,26</sup> and the sulfur-containing compounds react with Bi(OAc)\_3. The CASC process involved introducing a moderate number of seed



**Figure 3-1.** Schematics of CASC process. (a) Two-step CASC process. a-BiS<sub>x</sub> and c-Bi<sub>2</sub>S<sub>3</sub> represent amorphous and crystalline films after pre-thermal annealing and crystallization, respectively. Picture of the film is given. (b) Schematic showing how the seed crystal density affects the grain size. (c) Schematic showing the effect of the crystallization speed. Slow crystallization (right) prevents disordered crystal growth, resulting in a smooth surface.

crystals, as an excessive number would yield small-sized grains (Figure 3-1b). The resulting film was mostly amorphous (a-BiS<sub>x</sub>) without complete conversion to a crystalline phase, despite the presence of B<sub>2</sub>S<sub>3</sub> seed crystals inside the film. This was confirmed by the pale brown color and weak X-ray diffraction (XRD) pattern (*vide infra*) of a-BiS<sub>x</sub>. As reported for a bismuth-thiourea-chloride complex of (Bi[CS(NH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Cl<sub>3</sub>),<sup>27</sup> a similar complex with a reduced thiourea stoichiometry (*vide infra*) was presumably formed in the precursor solution. The lower crystallinity of the complex allowed for spin-coating of a smooth amorphous film.

The a-BiS<sub>x</sub> film was crystallized at an elevated temperature of 310 °C in a H<sub>2</sub>S/N<sub>2</sub> gas mixture. During ~30 min of gas-phase crystallization, the film was gradually converted to a multi-crystalline smooth Bi<sub>2</sub>S<sub>3</sub> thin film (see image in Figure 3-1a, c). The grain size was strongly dependent on the stoichiometry of the precursor solution, and Bi(OAc)<sub>3</sub>:thiourea in a 1:1.1 ratio was found to be optimal, while a 1:1.5 ratio yielded only small grains (Figure 3-2). In addition to the stoichiometry of Bi(OAc)<sub>3</sub> and thiourea (1:0.5–1.6), the following parameters were also examined: the environment (in air or a N<sub>2</sub>-glovebox), concentration (0.04–0.15 mol dm<sup>-3</sup>), temperature (120–165 °C), and time (20-120 s) of pre-thermal annealing; crystallization temperature of the furnace (280-360 °C); number of spin-coating steps (1–5); and H<sub>2</sub>S/N<sub>2</sub> gas temperature (25–260 °C) (see Experimental). During the optimization process, photoconductivity transients obtained by electrode-less flash-photolysis time-resolved microwave conductivity (TRMC) measurements served as an intuitive guide of the optoelectronic properties of the films.<sup>28</sup> Among the parameters listed above, the precursor stoichiometry and temperature had the largest impact on the TRMC transients. It should be noted that the CASC process is widely applicable to various substrates, including quartz, glass, silicon



**Figure 3-2.** AFM images of CASC-processed  $Bi_2S_3$  thin film obtained from different composition of the precursor.  $Bi(OAc)_3$ : thiourea = (a) 1 : 1.5 and (b) 1 : 1.1.

wafers with/without UV-ozone treatment, and mesoporous (mp-) $TiO_2$ , whereas the SILAR process requires a coarse surface such as mp- $TiO_2$  for deposition.

X-ray photoelectron spectroscopy (XPS) of the optimized  $Bi_2S_3$  film revealed peaks attributable to Bi 6s and S 2s orbitals (Figure 3-3), in agreement with previous reports.<sup>7, 14,24</sup> The calculated elemental ratio (Bi:S = 39.84:60.16) was in good agreement with the stoichiometry of  $Bi_2S_3$ , and no oxygen or nitrogen peaks were detected. Thus, the XPS results confirmed the high purity of CASC-processed  $Bi_2S_3$ .



**Figure 3-3.** XPS spectra of CASC-processed  $Bi_2S_3$  at (a) Bi 4f orbital, (b) S 2s orbital, and (c) O and N 1s orbital. The fitting curves are drawn along with experimental data. The ratio of Bi : S was calculated as 39.84 : 60.16, mostly identical to the theoretical stoichiometry of  $Bi_2S_3$ . No peak attributed to oxygen or nitrogen are not observed.

### 3-2-2. Structural orientation and morphology

Figure 3-4a shows XRD pattern of as-received Bi<sub>2</sub>S<sub>3</sub> powder, a pre-thermallyannealed film (a-BiS<sub>*x*</sub>), and a CASC-processed film (c-Bi<sub>2</sub>S<sub>3</sub>). A dramatic change from an amorphous to a highly-crystalline film was observed after gas-phase crystallization. The CASC film showed the most intense, sharp XRD pattern of all the films (Figure 3-4a, b). The correlation length of the crystallite at the (2 0 0) <sup>15,24</sup> peak (*d*-spacing = 0.56 nm) calculated using the Scherrer equation was largest for the CASC film (24 nm, Table 3-1). Interestingly, 2D-grazing incidence X-ray diffraction (2D-GIXD) results of the CASC film showed a more intense diffraction of the (2 0 0) peak in the out-of-plane direction than the in-plane direction (Figure 3-4c, d). These XRD results showed that the CASC film had a higher degree of 2D layer-stacking than did those prepared by other methods (Bi(EtXa)<sub>3</sub> and NPs). This is likely due to the slow, thermodynamically-favored



**Figure 3-4.** Crystallographic evaluations of  $Bi_2S_3$  films. (a) PXRD pattern of  $Bi_2S_3$  powder,  $Bi_2S_3$  films after pre-thermal annealing (a-BiS<sub>x</sub>), and after crystallization (c-Bi<sub>2</sub>S<sub>3</sub>) in CASC process. The dots represent the (2 0 0) diffraction. (b) PXRD patterns of Bi<sub>2</sub>S<sub>3</sub> films prepared by NPs spincoat, SP, CBD, SILAR, and Bi(EtXa)<sub>3</sub> spincoat. (c, d) 2D-GIXD images and profiles of Bi<sub>2</sub>S<sub>3</sub> films prepared by CASC, Bi(EtXa)<sub>3</sub>, and NPs. The white dots represent the (2 0 0) diffraction.  $q_{xy}$  and  $q_z$  are the scattering vectors along the xy and z planes, respectively. (e) Schematic of the stacked layer structures of Bi<sub>2</sub>S<sub>3</sub>. (f) UV-vis absorption spectra of a CASC-Bi<sub>2</sub>S<sub>3</sub> film. The inset is the Tauc plot to evaluate the band gap.

growth of 2D layers during crystallization of the CASC film. The observed layer structure illustrated in Figure 3-4e would merit charge carrier transport in the horizontal direction, as in a MoS<sub>2</sub>-based FET device.<sup>29,30</sup> An ultraviolet (UV)-visible absorption spectrum of the Bi<sub>2</sub>S<sub>3</sub> film displayed a broad feature extending to ~925 nm, the Tauc plot onset of which indicated a 1.39 eV bandgap (Figure 3-4f). The linear absorption coefficient at 900 nm and Urbach tail energy were  $1.7 \times 10^4$  cm<sup>-1</sup> (for either a direct<sup>8,31</sup> or indirect<sup>9</sup> transition) and 0.14 eV, respectively, which were inferior to those of LHPs (>10<sup>4</sup> cm<sup>-1</sup> and ~15 meV, respectively)<sup>32</sup>, however the wide coverage in the visible light region is promising for optoelectronic device applications.

	J 1 03	1	1 - 5		
Method	Morphology				
	Grain size (nm) <sup>a</sup>	$R_{\rm a}({\rm nm})^{\rm a}$	Correlation length (nm) <sup>b</sup>		
CASC	50-300	1.7	23.7		
Bi(EtXa) <sub>3</sub>	$50 \times 400$	47.3	17.4		
CBD	20–40	29.1	1.2		
SILAR	10–30	10.8	1.9		
SP	40–200	52.2	21.7		
NPs	5-20	3.5	7.3		

**Table 3-1.** Summary of morphology and photoresistor output of Bi<sub>2</sub>S<sub>3</sub> films.

<sup>a</sup> Evaluated from AFM height images of  $2 \times 2$  or  $1 \times 1 \mu m^2$ . <sup>b</sup> Evaluated from the (2 0 0) peaks of XRD patterns using the Scherrer relation.

The most pronounced effect observed for the CASC process was the improved AFM morphology (see Figure 3-5), which showed large, closely-packed crystal grains (with size L = 50-400 nm) with a root-mean-square surface roughness ( $R_a$ ) as small as 1.7 nm (Table 3-1). This was in sharp contrast to the trade-off observed in Bi<sub>2</sub>S<sub>3</sub> films prepared by conventional techniques; for NPs, a small  $R_a$  of 3.5 nm accompanied a small L of 5–20 nm, while for Bi(EtXa)<sub>3</sub> and SP, a large L (partly rod-like shapes) up to 400–500 nm gave a large  $R_a$  of 40–50 nm (Figure 3-5, Table 3-1). This was due to the two-step CASC process, consisting of amorphous film formation with a low seed level followed by slow crystallization, enabling separation of the nucleation and growth processes, which often occur simultaneously and uncontrollably. A SILAR-processed film exhibited a moderate L of 20–40 nm and  $R_a$  of 11 nm, however its inferior photoresponse associated with low crystallinity is a critical drawback for device applications.



**Figure 3-5.** AFM images of  $Bi_2S_3$  films prepared by (a) CASC process, (b)  $Bi(EtXa)_3$  spin-coating, (c) CBD, (d) SILAR, (e) SP, and (f) NPs. Note that the scale of figure (d) and (f) (a bar = 200 nm) is smaller than others (a bar = 400 nm), because of the small crystal grains.

## 3-2-3. Optoelectronic properties of Bi<sub>2</sub>S<sub>3</sub> thin films prepared by various process

The TRMC photoconductivity of Bi<sub>2</sub>S<sub>3</sub> films prepared by CASC and other methods were measured (Figure 3-6a, b). The optimized CASC film showed a  $\phi\Sigma\mu$  (see eq. 1-5 in Chapter 1) maximum ( $\phi\Sigma\mu_{max}$ ) of 1.3 ± 0.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at a reduced excitation light density (10<sup>12</sup> photons cm<sup>-2</sup> pulse<sup>-1</sup>) (Figure 3-6c, d). High  $\phi\Sigma\mu_{max}$  values of 1.65 and 0.95 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were also observed in the film from Bi(EtXa)<sub>3</sub> and as-received powder, respectively. In fact, the large TRMC signal observed for the powder sample was the basis of the initial motivation for developing the CASC process. The comparable  $\phi\Sigma\mu_{max}$  values of these films showcase their excellent optoelectronic response, consistent with the observed high crystallinities and large grain sizes. In contrast, the  $\phi\Sigma\mu_{max}$  values of films prepared by CBD, SILAR, SP, and NPs were two orders of magnitude smaller (< 10<sup>-2</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) than that of the CASC film. The low crystallinity and small grains comprising many lattice defects and/or impurities accounted for the low TRMC signals. Note that TRMC evaluation of a thermally-evaporated film failed, due to its extremely high steadystate conductivity arising from the inclusion of metallic bismuth. The  $\phi\Sigma\mu$  transients were also analyzed using a double exponential function. Analysis of the effective lifetime ( $\tau$ ) demonstrated that Bi(EtXa)<sub>3</sub> and CASC films had longer  $\tau$  values (20 and 13 µs, respectively) than the others (4.0–9.5 µs, Figure 3-6b). The short  $\tau$  values of Bi<sub>2</sub>S<sub>3</sub> prepared by other methods was likely due to degradation by carrier trapping in smallsized grains with high levels of impurities. Meanwhile, the high  $\phi\Sigma\mu$  and long  $\tau$  values observed for Bi(EtXa)<sub>3</sub> and CASC films appeared to be suitable for optoelectronic devices.



**Figure 3-6.** Comparative evaluation of Bi<sub>2</sub>S<sub>3</sub> using the TRMC technique. (a) TRMC transients of each sample ( $\lambda_{ex} = 500$  nm,  $I_0 = 10^{13}$  photons cm<sup>-2</sup>). (b) Effective lifetimes ( $\tau$ s) of the TRMC decays obtained by analysis with a double-exponential function: A<sub>1</sub>exp(-k<sub>1</sub>t) + A<sub>2</sub>exp(-k<sub>2</sub>t),  $\tau = (A_1(k_1)^{-1} + A_2(k_2)^{-1})(A_1 + A_2)^{-1}$ . (c) Dependence of TRMC transint maxima ( $\phi\Sigma\mu_{max}$ ) of CASC-Bi<sub>2</sub>S<sub>3</sub> on the excitation intensity ( $I_0$ ). (d) The kinetics at  $I_0 = 10^{11}$  photons cm<sup>-2</sup> to  $I_0 = 10^{15}$  photons cm<sup>-2</sup>.  $\lambda_{ex} = 500$  nm.

Long-range carrier transport in a device, which is complementary to the local charge carrier dynamics evaluated by electrode-less TRMC, is another crucial aspect. Thus, transient photocurrent (TPC) evaluations were performed in a simple device with two gold electrodes. Upon exposure to a nanosecond laser, the TPC intensity linearly increased with the applied bias (1–10 V), indicating ohmic contact between Bi<sub>2</sub>S<sub>3</sub> and the electrodes (Figure 3-7a–d). The schematics of TPC measurement is represented in Figure 3-7a. Interestingly, the TPC transients showed very slow decay rates of the order of several milliseconds, regardless of the preparation method. This was in contrast to the fast



**Figure 3-7.** TPC transients of Bi<sub>2</sub>S<sub>3</sub> films (prepared by (a) CASC, (b) Bi(EtXa)<sub>3</sub>, (c) SILAR, and (d) SP), (e) P3HT:PCBM, and (f) MAPbI<sub>3</sub> on mp-TiO<sub>2</sub> with the applied bias of 1–10 V. The inset is a schematic of a photoresistor device (the gap length is 0.5 mm).  $\lambda_{ex} = 355$  nm. Dependence of the (g) TPC maxima and (h) the number of charge (Q) calculated by integrating TPC transients over the time on the applied voltage for Bi<sub>2</sub>S<sub>3</sub> thin films (Bi(EtXa)<sub>3</sub>, CASC, SILAR, and SP), P3HT:PCBM, and MAPbI<sub>3</sub> on mp-TiO<sub>2</sub>.

TPC decay (0.41-1.1 ms) of emerging photovoltaic materials; a blend of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and a film of methylammonium cation (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, MA) lead iodide perovskite (MAPbI<sub>3</sub>) on mp-TiO<sub>2</sub> (Figure 3-7e, f). The slow TPC decay of Bi<sub>2</sub>S<sub>3</sub> was in line with the TRMC transients showing retarded charge recombination and slow relaxation (trapping). Most importantly, Bi(EtXa)<sub>3</sub> and CASC films demonstrated the highest TPC maxima over the entire applied bias; 2–3 orders of magnitude higher than those of P3HT:PCBM and Bi<sub>2</sub>S<sub>3</sub> prepared by SILAR and SP, and 10-fold higher than that of MAPbI<sub>3</sub> on mp-TiO<sub>2</sub> (Figure 3-7g). TPC evaluations of Bi<sub>2</sub>S<sub>3</sub> devices fabricated using CBD and NPs were not possible because of the large dark current due to excessive doping and low conductivity, respectively. The number of charges calculated by integrating the TPC over the elapsed time highlighted the superiority of Bi(EtXa)<sub>3</sub> and CASC over the others (Figure 3-7h).

# 3-2-4. Temperature-dependent measurements on CASC-processed Bi<sub>2</sub>S<sub>3</sub> film

To further understand the charge carrier transport mechanism in a CASC-Bi<sub>2</sub>S<sub>3</sub> film, the temperature dependence of the TRMC (Figure 3-8a, c) and TPC (Figure 3-8b, d) was evaluated. With decreasing temperature,  $\phi\Sigma\mu_{max}$  increased according to  $T^{-1.5}$  at 290–252 K, then decreased at 252–122 K. This indicated that the charge carriers obeyed band transport governed by phonon scattering near room temperature and hopping transport at low temperature, with activation energies (*E*<sub>a</sub>) of 140 meV (252–202 K) and 17 meV (202–122 K) obtained via following Arrhenius equation (3-1);

$$\mu = A \exp\left(-\frac{E_a}{kT}\right) \tag{3-1}$$

where  $\mu$  is charge mobility, A is scaling factor, and k is Boltzmann constant. The  $T^{-1.5}$  dependence at room temperature was consistent with the relatively large TRMC mobility  $(1.3 \pm 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ , assuming  $\phi = 1$ ). The same trends were observed in the temperature-dependent TPC, showing identical local and long-range carrier transport mechanisms. Remarkably, Hall effect measurements at room temperature revealed a moderate electron mobility of  $7.2 \pm 2.3 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$  along with an electron density (n) of  $(1.3 \pm 0.3) \times 10^{14} \text{ cm}^{-3}$  for the CASC film. n was five orders of magnitude lower than that of a thermally-evaporated Bi<sub>2</sub>S<sub>3</sub> film,<sup>7</sup> which is beneficial for dark current reduction in a device.



**Figure 3-8.** (a) TRMC and (b) TPC transients at low temperature. The colors and the arrows represent the decrease of the temperature.  $\lambda_{ex} = 355$  nm. Temperature dependence of (c) normalized TRMC maxima ( $\phi \Sigma \mu_{max}$ ) and (d) TPC maxima obtained from a) and b), respectively.

### **3-2-5.** Evaluation of photosensing property

Motivated by the observed heightened photoresponsivity of CASC-Bi<sub>2</sub>S<sub>3</sub>, it was utilized as photoresistor, a device used to detect steady-state light (sunlight or room light) by the change in conductance, allowing for automatic control of on-off switching of an external device such as a street light. A photoresistor has a simple device structure similar to that shown in Figure 3-7a (a commercial device has a pair of winding stripes to increase conductance). CdS has been widely used as the active layer, though the toxicity of Cd is a common issue, over which Bi<sub>2</sub>S<sub>3</sub> has a great advantage. The author evaluated current (*I*)-voltage (*V*) curves of a CASC-Bi<sub>2</sub>S<sub>3</sub> photoresistor with/without exposure to pseudo-sunlight (AM 1.5 G, 100 mW cm<sup>-2</sup>) or ambient room light from fluorescence tubes (Figure 3-9a). The photoconductance ( $\Delta G$ ) and on-off ratio (the ratio of conductance with/without light) were measured from the slope of the *I-V* curve and compared to other



**Figure 3-9.** Photoresistor characterization. (a) I-V curves of a CASC-Bi<sub>2</sub>S<sub>3</sub> film (gray solid line: photocurrent under pseudosunlight; gray dot line: photocurrent under room light; black solid line: dark current; black dot line: photocurrent under pseudosunlight after 1 month aging). (b) Plots of the photoconductance ( $\Delta G$ ) and on/off ratio of Bi<sub>2</sub>S<sub>3</sub> films prepared by various methods. Those of P3HT:PCBM and MAPbI<sub>3</sub> on mp-TiO<sub>2</sub> are also shown.

samples (Figure 3-9b). The obtained average  $\Delta G$  and on/off ratio of the CASC-Bi<sub>2</sub>S<sub>3</sub> photoresistor were as large as 0.21 µS and 4.6 × 10<sup>2</sup>, respectively - several orders of magnitude larger than those of other Bi<sub>2</sub>S<sub>3</sub> and P3HT:PCBM photoresistors (Table 3-2). The low  $\Delta G$  and on/off ratio of P3HT:PCBM photoresistors are considered as a result of insufficient charge separation due to low electric field intensity (~200 V / cm) in photoresistor device. The CASC photoresistor exhibited high sensitivity even for room light, with an on/off ratio of 8. Although a MAPbI<sub>3</sub> photoresistor performed similarly to the CASC photoresistor ( $\Delta G \sim 0.12 \mu$ S and on-off ratio  $\sim 7.0 \times 10^2$ ), the excellent stability of CASC-Bi<sub>2</sub>S<sub>3</sub> allowed the initial performance to be retained even after storage in air for one month (Figure 3-9a). Although Bi(EtXa)<sub>3</sub> and CBD films showed larger  $\Delta G$  values than did a CASC film, their on-off ratios were 1–3 orders of magnitude lower, due to the large dark current. In contrast, the CASC film achieved both large photoconductance and high on-off ratio, making them most suitable for light sensing applications.

Upon periodic illumination (515 nm, ~1 Hz), CACS-Bi<sub>2</sub>S<sub>3</sub> exhibited good photoswitching with the prompt rise and slow decay times of 0.02 and 0.06 s, respectively (Figure 3-10, the former is close to the instrumental response function). The figures-of-merit of photodetector, i.e. responsivity (*R*), external quantum efficiency (EQE), and detectivity (*D*\*) were evaluated for the Bi<sub>2</sub>S<sub>3</sub> photoresistors according to the reported procedure (see Experimental).<sup>29</sup> Although the *R* ( $2.4 \times 10^{-3}$  A W<sup>-1</sup>) and EQE (0.58%) of

CASC-Bi<sub>2</sub>S<sub>3</sub> were lower than those of Bi(EtXa)<sub>3</sub> film ( $R = 5.4 \times 10^{-2}$  A W<sup>-1</sup>, EQE =13%) due to the lower photocurrent (Table 3-2),  $D^*$  of the former was much larger than that of the latter owing to the excellent on/off ratio. Note that R, EQE, and  $D^*$  are dependent on the applied bias, wavelength, and light power density,<sup>29,30</sup> in particular, the gap length of electrodes. Nonetheless, the large  $D^*$  (1.7 × 10<sup>11</sup> Jones) of CASC-Bi<sub>2</sub>S<sub>3</sub> comparable to



**Figure 3-10.** (a) Photoresponse of the CASC-Bi<sub>2</sub>S<sub>3</sub> photoresistor upon exposure to a CW laser ( $\lambda = 515$  nm) through a mechanical chopper (~1 Hz). A termination: 50  $\Omega$ . (b) Expanded signal of the photoresponse. (c) Photoresponse of a Si photodiode, which can be assumed as an instrumental response function (the rise and decay of signals are caused by the edge part of chopper slit, not due to the response time of a Si photodetector). A termination: 50 $\Omega$ .

**Table 3-2.** Summary of photoresistor output (photoconductance ( $\Delta G$ ), on-off ratio, responsivity, external quantum efficiency (EQE), and detectivity ( $D^*$ )) of Bi<sub>2</sub>S<sub>3</sub> films.

Method	$\Delta G$	On/off	Responsivity	EQE	$D^*$
	(µS) <sup>a</sup>	ratio <sup>a</sup>	$(A W^{-1})^{b}$	(%) <sup>b</sup>	$(10^{10} \text{ Jones})^{b,c}$
CASC	$2.1 \times 10^{-1}$	460	$2.4  imes 10^{-3}$	0.58	17
Bi(EtXa) <sub>3</sub>	2.1	78	$5.4 imes10^{-2}$	13	6.4
CBD	3.4	1.9	$8.9 imes10^{-2}$	21	1.3
SILAR	$8.7 \times 10^{-3}$	12.5	$1.4  imes 10^{-3}$	0.34	1.2
SP	$4.8 \times 10^{-4}$	2.5	$1.1  imes 10^{-4}$	$2.7  imes 10^{-2}$	2.6
NPs	$5.4 \times 10^{-5}$	1.1	$2.9  imes 10^{-5}$	$7.0 imes10^{-3}$	1.3

<sup>a</sup> Evaluated from the slope of the I–V curves of photoresistors under pseudo-sunlight (AM 1.5 G, 100 mW cm<sup>-2</sup>). <sup>b</sup> Evaluated from the currents of photoresistors at 10 V with/without monochromatic light (512 nm, 0.95 mW cm<sup>-2</sup>). The gap distance and length of electrodes were 0.5 mm and 3 mm, respectively. Note that responsivity and EQE are varied by the gap distance, the light wavelength, and the light power density. <sup>c</sup> 1 Jones = 1 cm Hz<sup>1/2</sup> W<sup>-1</sup>

the reports found in high-sensitive heterojunction  $Bi_2Te_3$  photodetectors (10<sup>10</sup>-10<sup>11</sup> Jones)<sup>29,30,33</sup> is notable.

Solution-processable bismuth-based semiconductors have emerged as viable alternatives to lead-based photovoltaics. These include MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> processed from DMSO,<sup>34</sup> AgBi<sub>2</sub>I<sub>7</sub> from *n*-butylamine,<sup>35</sup> and colloidal nanocrystals of AgBiS<sub>2</sub> from toluene,<sup>36</sup> which reportedly show PCEs of 1, 1.2, and 6.3%, respectively. Antimony chalcogenides of Sb<sub>2</sub>S<sub>3</sub> prepared by CBD (PCE = 7.5%)<sup>37</sup> and thermally-evaporated Sb<sub>2</sub>Se<sub>3</sub> (PCE = 5.6%)<sup>38</sup> are notable analogues of Bi<sub>2</sub>S<sub>3</sub>. The author applied a preliminary CASC process to lead sulfide (PbS) and obtained a film with large grains (~100 nm), a small  $R_a$  (6.3 nm), and a large TRMC signal ( $\phi\Sigma\mu_{max}$  of 0.45 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>), comparable to those of Bi<sub>2</sub>S<sub>3</sub> (Figure 3-11). Therefore, the CASC process shows great promise for advanced solution-processed metal sulfide semiconductors.



**Figure 3-11.** (a) AFM image of the PbS film.  $R_a = 6.3$  nm. (b) TRMC transient of a PbS film prepared by CASC process.

# 3-3. Conclusion

In conclusion, the author successfully developed a CASC process for the preparation of high quality Bi2S3 thin films, consisting of facile spin-coating and crystallization steps. Thiourea was used in the precursor solution as a sulfurization source upon pre-thermal annealing, as well as a chemical mediator to fabricate a smooth, amorphous film with the lack of sulfur. Subsequent gas-phase crystallization lead to a high degree of crystallinity and purity with the expected elemental stoichiometry and a 2D layer-stacked structure. Importantly, the CASC process simultaneously achieved excellent film morphology (low surface roughness and large grain size), high TRMC/TPC signal strength with band transport at room temperature, and moderate Hall effect electron mobility. The CASC photoresistor demonstrated superior performance (photoconductance, on-off ratio, and detectivity) over other Bi<sub>2</sub>S<sub>3</sub> devices prepared by conventional methods. The high stability and non-toxicity are also attractive features, making the CASC method promising for fabricating optoelectronic devices from metal sulfide materials.

# **3-4.** Experimental

### Materials and general measurements

Bi(OAc)<sub>3</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>, BiI<sub>3</sub>, and BiCl<sub>3</sub> were purchased from Sigma-Aldrich. Thiourea and propionic acid were purchased from Tokyo Chemical Industry. Super dehydrated grade DMSO and toluene were purchased from Wako Chemical Industries Ltd. These chemicals were used without further purification. Steady-state photoabsorption spectroscopy was performed using a Jasco V-730 UV-vis spectrophotometer. PYS experiments were performed using a Bunko Keiki BIP-KV202GD. AFM observations and thickness measurements were performed using a Bruker Innova and a Bruker Dektak XT, respectively. XPS evaluations were performed using a Shimadzu AXIS-165x. XRD data were collected on a Rigaku MiniFlex-600 instrument using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 1.54187 Å) at room temperature in air. 2D-GIXD experiments were conducted on the BL46XU beamline at SPring-8 (Japan Synchrotron Radiation Research Institute, JASRI), using 12.39 keV ( $\lambda = 1$  Å) X-rays. Hall effect mobilities were evaluated using a Toyo Resitest8303 and the van der Pauw method under an applied magnetic field of 0.66 T in air at room temperature. The Hall carrier concentration (n) and Hall mobility ( $\mu$ ) were calculated from the Hall coefficient  $(R_{\rm H})$  by assuming a single-band model and a Hall factor of 1, i.e.  $n = (eR_{\rm H})^{-1}$  and  $\mu = \sigma R_{\rm H}$ , where e is the elementary charge and  $\sigma$  is the conductivity.

## Preparation of CASC-Bi<sub>2</sub>S<sub>3</sub> films and other films

The optimized CASC process was performed as follows: Bi(OAc)<sub>3</sub> (0.1 M) and thiourea (0.11 M) were dissolved in propionic acid and stirred for 30 min at 50 °C. This precursor solution was then filtrated (0.20 µm), spin-coated (2500 rpm, 20 s) onto a cleaned substrate after UV-ozone treatment (10 min), and subjected to pre-thermal annealing at 150 °C for 50 s. The spin-coating and annealing steps were repeated three times to produce a film with a thickness of 60 nm. These processes were performed in a N<sub>2</sub> glovebox (O<sub>2</sub> < 0 ppm, H<sub>2</sub>O < 0.0 ppm). The obtained film was then transferred into a glass pipe chamber (3.0 cm in inner diameter, 40 cm in length) equipped with a cylindrical muffle heater and thermally annealed (with a heater temperature of 330 °C and measured substrate temperature of 310 °C) under a flow of mixed gases (H<sub>2</sub>S:N<sub>2</sub> =1:3) for 20 min. The gas flow was initiated when the chamber temperature reached 200 °C, with an initial flow rate of 300 mL min<sup>-1</sup> for 2 min, followed by a decrease to 100 mL min<sup>-1</sup>. Details on the gas flow and temperature are given in Figure 3-12. The optimization of each condition such as precursor composition, annealing temperature, etc. were conducted with TRMC

evaluation (Figure 3-13). PbS film was prepared by the same manner as  $Bi_2S_3$ . The precursor solution involved Pb acetate (0.1 M) and thiourea (0.11 M) dissolved in propionic acid. For comparative studies,  $Bi_2S_3$  thin films were prepared according to reported procedures for SILAR,<sup>19</sup> CBD,<sup>17</sup> NPs,<sup>10</sup> Bi(EtXa)<sub>3</sub>,<sup>23</sup> and SP<sup>21</sup>. These were deposited on a cleaned quartz substrate for TRMC or a cleaned glass substrate for TPC and photoresistors. Note that SILAR required an underlying mp-TiO<sub>2</sub> layer, as a film was not able to be formed on a bare substrate. A MAPbI<sub>3</sub> film (300 nm in thickness) was prepared on a mp-TiO<sub>2</sub> layer in a N<sub>2</sub> glovebox by spin-coating a 1.0 M DMSO solution, along with toluene anti-solvent treatment and thermal annealing at 110 °C for 10 min. A P3HT:PCBM = 1:1 (wt/wt) film (200 nm in thickness) was prepared by spin-coating (at 2000 rpm for 20 s, slope 2 s) a 1.5 wt% chlorobenzene solution. The film was thermally annealed at 150 °C for 10 min. All procedures were conducted in a N<sub>2</sub> glovebox.



**Figure 3-12.** Profile of crystallization temperature and gas flow rate. Gas-flow rate (drawn by blue) was precisely controlled by using a mass-flow controller (KOFLOC; 8500MC-0-1-2). The heater temperature measured with a thermocouple is provided. The temperature of a substrate in a glass pipe chamber was measured to be 310 °C when the heater temperature was 320 °C. Before starting gas-flow, the glass pipe chamber was purged by nitrogen.


**Figure 3-13.** Screening of processing parameters by using TRMC. (a) The composition of precursor solution  $(Bi(OAc)_3 : thiourea = 1:0.5-1.6)$ , (b) environment of spin-coating and pre-thermal annealing (in the air or a N<sub>2</sub>-glovebox), (c) the concentration (0.04–0.15 mol dm<sup>-3</sup>), (d) temperature (120–165°C, blue line) and time (20–120 s, red line) of pre-thermal annealing, (e) crystallization temperature (280–360°C), (f) the number of spin-coating (1–5 times), and (g) the initial temperature to start flowing H<sub>2</sub>S/N<sub>2</sub> gas (25–260°C).

### Flash-photolysis TRMC

Thin films were prepared on a quartz plate. The sample was set in a resonant cavity and probed by continuous microwaves at ca. 9.1 GHz. The laser excitation from an optical parametric oscillator (OPO, Continuum Inc., Panther) seeded by third harmonic generation of a Nd:YAG laser (Continuum Inc., Surelite II, 5–8 ns pulse duration, 10 Hz) was set at 500 nm. The photon density ( $I_0$ ) varied from  $1.28 \times 10^{11}$ – $6.42 \times 10^{14}$  photons cm<sup>-2</sup> pulse<sup>-1</sup>. The photoconductivity transient  $\Delta\sigma$  was converted to  $\phi\Sigma\mu$  via the eq. 1-5 in

Chapter 1. For low-temperature experiments, a cavity with a sample was set in a vacuum chamber with an electric cooler. Other experiments were conducted at room temperature in air.

## TPC and photoresistor

The films were prepared on a cleaned glass substrate by the above-mentioned procedures (SILAR and MAPbI<sub>3</sub> films were prepared on mp-TiO<sub>2</sub>/glass). A pair of rectangular gold electrodes (0.5 mm gap, 1 mm width and 3 mm length) was deposited through a shadow mask by thermal evaporation in a vacuum chamber ( $10^{-5}$  Pa). TPC transients induced by exposure to third-harmonic generation (THG: 355 nm) of a Nd:YAG laser ( $I_0 = 1.82 \times$ 10<sup>13</sup> photons cm<sup>-2</sup> pulse<sup>-1</sup>) were measured using an oscilloscope (Tektronix model DPO4000 with a 3 k $\Omega$  termination) under an external bias (0–10 V: 1 V steps) applied using a source meter (Keithley model 2612A). For the low-temperature experiments, a device was set in a vacuum chamber with an electric cooler. Other experiments were conducted at room temperature in air. Photoresponse under periodic illumination was measured using an oscilloscope and an attenuated CW laser (Spectra-Physics Inc., EXLSR-515-50S-W, 515 nm) through a mechanical chopper (~1 Hz). I-V curves of photoresistors (using the same device as for TPC measurements) were measured by sweeping the voltage (from -10 to +10 V) of the source meter under AM 1.5 G solar illumination at 100 mW cm<sup>-2</sup> (1 sun, monitored by a calibrated standard cell, Bunko Keiki SM-250 KD) from a 300 W solar simulator (SAN-EI Corp., XES-301S). Responsivity (R), external quantum efficiency (EQE), and detectivity  $(D^*)$  were evaluated from the current of photoresistor at 10 V with/without monochromatic light (512 nm, 0.95 mW cm<sup>-2</sup>) from a Xe lamp (Asahi Spectra Corp., MAX-303) through a band-pass filter ( $\Delta \lambda =$ 7 nm). These parameters were calculated according to the report, <sup>29</sup> through  $R = I_P (PA)^{-1}$ , EQE =  $(I_phv)(qPA)^{-1}$ , and  $D^* = (AR (2qI_d)^{-1})^{1/2}$ , where  $I_p$  is the photocurrent,  $I_d$  is the dark current, P is the light power density, A is the active area, h is the Planck constant, v is the photon frequency, and q is the elementary charge.

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# **Chapter 4: Comparative Study of Charge Carrier Dynamics in Bismuth Dimer and Double Perovskite**

# 4-1. Introduction

Bismuth-based halide semiconducting materials such as dimer structure of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>  $(A = Cs^+, CH_3NH_3^+ (MA), (CH_3)_2NH^+ (FA))$  and double perovskite (DP) of Cs<sub>2</sub>AgBiBr<sub>6</sub> have been widely investigated for photovoltaic application. Park et al. performed a theoretical and experimental study on the dimer  $A_3Bi_2I_9$  (A = Cs<sup>+</sup>, MA) solar cells.<sup>1</sup> Pazoki, et al. reportedly showed the large carrier effective mass and exciton binding energy of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> by theoretical calculation.<sup>2</sup> Shin, et al. demonstrated 0.71% PCE for Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> by solvent engineering and device structure optimization.<sup>3</sup> On the other hand, 3dimensional (3D) DPs such as Cs<sub>2</sub>AgBiBr<sub>6</sub> are claimed to exhibit better charge transport property than A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> dimer structures, owing to the band-like transport.<sup>4,5</sup> Indeed, Cs<sub>2</sub>AgBiBr<sub>6</sub>-based solar cells have exhibited the higher PCE of 2.23% than A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>-based solar cells.<sup>4</sup> However, the PCE is still much lower than the theoretical limit of 7.92% calculated from the spectral integration and assumed small voltage loss.<sup>6</sup> A low photocurrent density is presumably due to the large effective mass of charge carrier and giant electron-phonon coupling.<sup>7</sup> However, direct observation of charge carrier generation, transport, and transfer process including non-radiative recombination are mostly unexplored in these materials.

In this chapter, it is described that the dynamics of photogenerated charge carrier were investigated by using TRMC measurement.<sup>8,9</sup> Photoconductivity and charge carrier transport /transfer from A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> or Cs<sub>2</sub>AgBiBr<sub>6</sub> to electron transport material (ETM) and hole transport material (HTM) were comparatively evaluated, which showed a good correlation with the solar cell performance. The obtained results contribute to understanding the potential optoelectronic performance of bismuth-based halide materials.

# 4-2. Results and discussion

# 4-2-1. Charge transport property evaluated by TRMC

Thin films of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and Cs<sub>2</sub>AgBiBr<sub>6</sub> were prepared by simple spin-coating and thermal annealing of precursor solution (see Experimental). XRD pattern of each film showed a good agreement with the previous reports,<sup>3,4</sup> indicating that crystal structures of prepared film samples are expected dimer or DP (Figure 4-1a). The resultant crystal structures of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> (A = Cs, MA, FA) and Cs<sub>2</sub>AgBiBr<sub>6</sub> are shown in Figure 4-1b and c, respectively. The bandgap energies ( $E_g$ ) were determined from the onset of UV-vis absorption spectra, where absorption edges of Tauc plot (n = 2) correspond to the direct transition (Figure 4-1d).<sup>29</sup> The determined  $E_g$  were Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>: 2.05 eV, MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>: 2.16 eV, FA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>: 2.20 eV, and Cs<sub>2</sub>AgBiBr<sub>6</sub>: 2.37 eV. If Cs<sub>2</sub>AgBiBr<sub>6</sub> is regarded as an indirect transition material as reported previously,<sup>11</sup> its  $E_g$  is 2.20 eV from the Tauc plot of n = 1/2. These results are also consistent with the literature,<sup>11</sup> which further supports the appropriate preparation of the films. Emission was too small to be detected in fluorescence spectrometer.



**Figure 4-1.** (a) XRD patterns of FA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, and Cs<sub>2</sub>AgBiBr<sub>6</sub> thin films. Schematic image of crystal structure of (b) A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and (c) Cs<sub>2</sub>AgBiBr<sub>6</sub>. (d) Tauc plots of film samples obtained from photoabsorption spectra. The inset is the original absorption spectra.

TRMC measurements of dimer A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> were carried out for the single layer films (single), bilayer films (*n/i*) composed of mp-TiO<sub>2</sub> as n-type ETM and A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> as the intrinsic (*i*) layer, and triple layer films (*n/i/p*) composed of mp-TiO<sub>2</sub>, A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, and Poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) as p-type HTM (Figure 4-2a). The single layer films showed very similar TRMC transients among the samples (Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, and FA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>) in both  $\phi\Sigma\mu$  maxima ( $\phi\Sigma\mu_{max}$ ) of (1–2) × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and decay speed (Figure 4-2b–d). The *n/i* films showed distinct increase of  $\phi\Sigma\mu_{max}$  and



**Figure 4-2.** (a) Schematics of film sample for TRMC measurement. TRMC transients of (b) Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, (c) MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, (d) FA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, and (e) Cs<sub>2</sub>AgBiBr<sub>6</sub> thin films. The fitting curves are drawn by double exponential functions:  $A_1 \exp(-k_1t) + A_2 \exp(-k_2t)$ . The effective lifetime ( $\tau$ ) was calculated by  $(A_1/k_1 + A_2/k_2)/(A_1 + A_2)$ . The colors and line shape of fitting curves correspond to the sample structure; single *i* layer (gray dot line), n/i layer (black dot line), and n/i/p layer (black solid line).

Materials	$\phi \Sigma \mu_{ m max}$	$(\times 10^{-4} \text{ cm})$	$^{2} \mathrm{V}^{-1} \mathrm{s}^{-1}$ )	τ (μs)			
	single	n/i	n/i/p	single	n/i	n/i/p	
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	2.0	2.5	2.8	0.61	0.75	1.8	
$MA_3Bi_2I_9$	2.0	4.2	5.0	1.2	2.4	3.3	
FA3Bi2I9	1.2	3.6	4.0	0.97	1.7	2.0	
Cs <sub>2</sub> AgBiBr <sub>6</sub>	38	110	78	0.13	0.26	0.16	

**Table 4-1.** Summary of  $\phi \Sigma \mu_{max}$  and effective lifetime ( $\tau$ , see Figure 4-2) obtained from double exponential fitting.

effective lifetime ( $\tau$ ) compared with the single layers (Table 4-1). This is explained by electron transfer from A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> to mp-TiO<sub>2</sub> and retarded charge recombination, where the electron mobility in A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> is assumed much smaller than that in TiO<sub>2</sub> ( $-10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>12</sup> It should be noted that the increase of  $\phi\Sigma\mu_{max}$  was insignificant without HI addition. Although electron transfer to mp-TiO<sub>2</sub> was observed, the increase of  $\phi\Sigma\mu_{max}$  from single layer to n/i layer was insignificant (from (1.2–2.0) × 10<sup>-4</sup> to (2.5–4.2) × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), which is much lower than electron mobility in TiO<sub>2</sub> ( $-10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>12</sup> This would suggest the inefficient electron transfer to TiO<sub>2</sub>. Similarly, hole transfer was examined by comparing TRMC signals of n/i layer and n/i/p layer, showing the increase of  $\phi\Sigma\mu_{max}$  as small as 0.1–0.2 times. Therefore, hole transfer is also inefficient and/or TRMC hole mobility of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> is comparable to that of PTAA ( $-10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>13</sup> Despite the low hole/electron transfer, the charge recombination is suppressed to some extent, which would merit the solar cell performance. In addition, A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> suffers from a large exciton binding energy, short carrier diffusion length, and high trap state density,<sup>4</sup> in accordance with the low score of the TRMC evaluation.

Besides, the single layer of Cs<sub>2</sub>AgBiBr<sub>6</sub> DP showed much higher  $\phi \Sigma \mu_{max}$  of  $3.8 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> than A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> dimer (Figure 4-2d). This is possibly associated with the 3D crystal structure of Cs<sub>2</sub>AgBiBr<sub>6</sub> that leads to a small exciton binding energy and high charge carrier mobility.<sup>4</sup> However, the  $\tau$  of TRMC transient of Cs<sub>2</sub>AgBiBr<sub>6</sub> (0.13 µs) is much shorter than those of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> (~1 µs). After compositing with mp-TiO<sub>2</sub>, the  $\phi \Sigma \mu_{max}$  of Cs<sub>2</sub>AgBiBr<sub>6</sub> exhibited a notable increase in the  $\phi \Sigma \mu_{max}$  (from  $3.8 \times 10^{-3}$  to  $1.1 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), and the  $\tau$  was extended by two times, owing to more efficient electron transfer than A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>. In contrast, the  $\phi \Sigma \mu_{max}$  of n/i/p layer was decreased compared with that of n/i layer, which opposes to A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>. This suggests that Cs<sub>2</sub>AgBiBr<sub>6</sub> has a higher hole mobility than PTAA. Note that low  $\phi$  (<<1) of Cs<sub>2</sub>AgBiBr<sub>6</sub> limits  $\phi \Sigma \mu_{max}$ . This is the origin of lower  $\phi \Sigma \mu_{max}$  of n/i/p Cs<sub>2</sub>AgBiBr<sub>6</sub> (~8 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) than the hole mobility of PTAA (~10<sup>-1</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).

Regardless of the layer structure (single, n/i, and n/i/p), MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> showed greater  $\phi \Sigma \mu_{max}$  and  $\tau$  than Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and FA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, suggestive of superior solar cell performance of MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> to Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and FA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>. Remarkably, Cs<sub>2</sub>AgBiBr<sub>6</sub> displayed more increased  $\phi \Sigma \mu_{max}$  than MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, and thus it should show the highest PCE in these pseudoperovskites. Note that  $\phi \Sigma \mu_{max}$  of high-performing MAPbI<sub>3</sub> is extremely large (~70 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and shows nearly 100% electron and hole transfer efficiencies from MAPbI<sub>3</sub> to mp-TiO<sub>2</sub> and PTAA.<sup>14</sup> Based on these facts, Cs<sub>2</sub>AgBiBr<sub>6</sub> is still unable to compete with MAPbI<sub>3</sub>.

#### 4-2-2. Solar cell performance

Consequently, photovoltaic devices with a normal structure (FTO/compact TiO<sub>2</sub>/mp-TiO<sub>2</sub> /absorber/PTAA (doped)/Au) were prepared (Figure 4-3a). According to the energy diagram obtained from PYS and Tauc plot, all absorbers have downhill energy levels of VBM and conduction band minimum (CBM) relative to HTL and ETL, respectively (Figure 4-3b). In spite of the energy level matching, A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>-based devices showed a poor short circuit current density ( $J_{SC}$ , ~0.11 mA cm<sup>-2</sup>), which strictly limited the PCE (< 0.016%) (Table 4-2). The external quantum efficiency (EQE) spectra also



**Figure 4-3.** (a) Schematic of a layered photovoltaic device. (b) Energy diagram of each layer obtained from PYS and UV-vis measurement. (c) EQE spectra of each devices. *J-V* curve of photovoltaic devices based on  $A_3Bi_2I_9$  (A = (d) Cs, (e) MA, and (f) FA) and (g) Cs<sub>2</sub>AgBiBr<sub>6</sub>.

	$J_{ m SC}$	Voc	FF	Rs	$R_{ m Sh}$	PCE
	$(mA cm^{-2})$	(V)		$(\Omega \text{ cm}^2)$	$(k\Omega \ cm^2)$	(%)
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.076	0.40	0.38	100	11	0.012
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.11	0.34	0.42	20	7.4	0.016
FA3Bi2I9	0.068	0.45	0.39	1000	14	0.012
Cs <sub>2</sub> AgBiBr <sub>6</sub>	1.2	0.92	0.64	40	7.3	0.72

 Table 4-2. Summary of best-performed device performance.

show very low values for  $A_3Bi_2I_9$  (Figure 4-3c). Their PCE and  $J_{SC}$  were even lower without HI processing. These results are consistent with the TRMC evaluations, which showed the small  $\phi\Sigma\mu_{max}$  and low charge transfer efficiency to ETL and HTL. Despite insignificant leak current (Figure 4-3d-f), a large open circuit voltage loss (~1.89 eV) and low fill factor (~0.42) are observed. This might result from a high trap density<sup>15</sup> and large offset between VBM of  $A_3Bi_2I_9$  and HOMO of PTAA.

Meanwhile,  $Cs_2AgBiBr_6$ -based device afforded more than 10-fold higher  $J_{SC}$  (1.2) mA cm<sup>-2</sup>) compared with the A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>-based devices. This is also consistent with the high  $\phi \Sigma \mu_{max}$  and charge transfer efficiency observed in TRMC evaluation. In addition, Cs<sub>2</sub>AgBiBr<sub>6</sub>-based device showed smaller V<sub>OC</sub> loss (~1.46 eV) and higher FF value (~0.64), which suggests a less trap state density than A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>. However, the obtained PCE is still considerably lower than theoretical limit (7.92%),<sup>5</sup> suffering from the limited current density. The significantly small  $J_{SC}$  compared to the integration of solar spectrum up to the bandgap (~8 mA cm<sup>-2</sup>) is probably caused by the low  $\phi$  value due to inefficient charge separation and the limited charge carrier transfer as revealed in TRMC evaluation. To quantify the  $\phi$  value for further discussion, transient photocurrent (TPC) measurement and charge extraction (CE) measurement appears to promising way, where generated charge density (n) and bimolecular recombination current density ( $J_{bi}$ ) is obtained.<sup>17-19</sup> The hysteresis in J-V curve (forward: 0.69%, reverse: 0.76%) is not so small, which is frequently considered as a result of ion migration in perovskite solar cells.<sup>16</sup> Anti-solvent treatment which is not used in the study described in this chapter is expected to decrease vacancies responsible for the hysteresis.

# 4-3. Conclusion

The charge carrier dynamics in A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> dimer (A = Cs<sup>+</sup>, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, and HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>) and Cs<sub>2</sub>AgBiBr<sub>6</sub> DP were studied by TRMC evaluation. Cs<sub>2</sub>AgBiBr<sub>6</sub> single layer film showed a relatively high TRMC signal compared with A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> owing to the higher electron and hole mobility. In addition, Cs<sub>2</sub>AgBiBr<sub>6</sub>/mp-TiO<sub>2</sub> bilayer showed the greater increase of  $\phi \Sigma \mu_{max}$  (1.1 × 10<sup>-2</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) than A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>/mp-TiO<sub>2</sub> bilayer. This indicates a higher electron transfer efficiency in the former. However, the electron and hole transfer efficiencies were not high enough compared to the high-performing MAPbI<sub>3</sub>. The obtained device performance, especially current density, showed a good agreement with TRMC evaluation. Despite the limited potential of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> and Cs<sub>2</sub>AgBiBr<sub>6</sub> as the light absorber, this result provides a rational step for exploring forthcoming lead-free perovskites. Based on the insight, further material exploration is desired.

# 4-4. Experimental

# Materials and film preparation

CsI, MAI, FAI were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. CsBr, BiI<sub>3</sub>, BiBr<sub>3</sub> were bought from Sigma-Aldrich Co., Ltd. All chemicals were used without further purification. A 0.5 M precursor solution of  $A_3Bi_2I_9$  and  $Cs_2AgBiBr_6$  (molar fraction) was prepared in a N<sub>2</sub>-filled glovebox by dissolving 0.5 mmol of BiI<sub>3</sub> or BiBr<sub>3</sub> and stoichiometric amount of AX (A = Cs, MAI, FAI, X = I, Br) into 1 mL dimethyl sulfoxide (DMSO). 40 µL HI aqueous solution (54 wt%, TCI) was added to  $A_3Bi_2I_9$  solution to increase solubility and improve film quality. The precursor solution was spin-coated onto a substrate with/without mesoporous (mp) TiO<sub>2</sub> at 2,000 rpm for 30 s. The obtained films were subsequently annealed at 110 °C for  $A_3Bi_2I_9$  and 250 °C for  $Cs_2AgBiBr_6$  for 10 min. For the observation of hole transfer, a toluene solution (10 mg/mL) of poly(triarylamine) (PTAA) with Li-dopant (Li-TFSI) was spin-coated onto the  $A_3Bi_2I_9$  or  $Cs_2AgBiBr_6$  film. These procedures were operated inside the glovebox.

## Film characterization

Valence band maxima (VBM) was measured by photoelectron yield spectroscopy (PYS) using a Bunko Keiki Corp. BIP-KV201 (accuracy:  $\pm 0.02$  eV, extraction voltage = 10 V) in a vacuum (<10<sup>-2</sup> Pa). The film was prepared onto a F-doped SnO<sub>2</sub> (FTO) layer on a glass substrate, which was contacted through aluminum tape and an Au-coated electrode. X-ray diffraction (XRD) was performed by using a Rigaku Corp. MiniFlex-600 instrument (Cu K $\alpha$  radiation:  $\lambda = 1.54$  Å) in the air at room temperature. Photoabsorption spectra were measured using a Jasco Corp. V-730.

## TRMC

A thin film was prepared on a quartz plate. The sample was set in a resonant cavity and probed by continuous microwaves at ca. 9.1 GHz. The excitation laser (500 nm) from an optical parametric oscillator (OPO, Continuum Inc., Panther) seeded by the third harmonic generation of a Nd:YAG laser (Continuum Inc., Surelite II, 5–8 ns pulse duration, 10 Hz) was used as the excitation. The photon density ( $I_0$ ) was changed from  $6.4 \times 10^{14}$  to  $2.6 \times 10^{15}$  photons cm<sup>-2</sup> pulse<sup>-1</sup>. The photoconductivity transient  $\Delta\sigma$  was converted to  $\phi\Sigma\mu$  via the eq. 1-5 in Chapter 1.

## Device fabrication

An FTO substrate was cleaned with detergent, acetone, isopropyl alcohol, and deionized water, a compact TiO<sub>2</sub> layer was deposited onto the FTO/glass by spray pyrolysis using a solution of titanium diisopropoxide bis(acetylacetonate) (Sigma Aldrich) in ethanol (1:40 v/v) at 500 °C. The substrate was immersed in a 50 mM aqueous solution of TiCl<sub>4</sub> (Wako Chemical Industries Ltd.) for 30 min, followed by rinsing with deionized water and sintering at 500 °C for 20 min. A 200 nm-thick mp-TiO<sub>2</sub> layer was deposited onto the compact TiO<sub>2</sub> layer by spin-coating (5,000 rpm, 30 s) of a diluted TiO<sub>2</sub> paste (PST–18NR, JGC Catalysts and Chemicals Ltd.) in ethanol (paste/ethanol = 1:7 w/w), followed by sintering at 500 °C for 20 min. A precursor solution was spin-coated at 2,000 rpm for 30 s onto a substrate, followed by annealing at 100 °C for 10 min. A PTAA toluene solution with Li-TFSI (PTAA : Li-TFSI = 1 : 0.15) was spin-coated (4,000 rpm, 30s) as HTL. Subsequently, a 100 nm-thick gold anode was thermally deposited in a vacuum chamber.  $R_s$  and  $R_{sh}$  values were calculated from the inverse of the slope of *JV* curve at  $V = V_{OC}$  and V = 0, respectively.

# 4-5. Reference

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# **Chapter 5: Optoelectronic and Energy Level Exploration of Biand Sb-Based Photoabsorber**

# 5-1. Introduction

There are numerous crystal structures of Bi- and Sb-based materials as described in Chapter 1. The most primitive one is  $A_3M_2X_9$ ,<sup>1–7</sup> with dimer or layered crystal structures (Figure 1-7a in Chapter 1), though the dimer such as  $A_3Bi_2I_9$  (A = Cs, MA, FA) would be detrimental to the exciton diffusion and efficient charge transport,<sup>8</sup> resulting in a low PCE (Chapter 4).<sup>9</sup> Besides, other halide materials such as silver bismuth iodide (e.g., AgBiI4)<sup>10–12</sup> and the A<sub>2</sub>MM'X<sub>6</sub> DPs<sup>13–16</sup> (Figure 1-7b, c), chalcogenide materials<sup>24–27</sup> (Figure 1-7d), and chalcohalide materials such as rod-like MSX<sup>17–20</sup> and AMSX<sub>2</sub> splitanion perovskites (SAPs) (Figure 1-7e, f)<sup>21–23</sup> are also notable. However, a comprehensive evaluation and comparison of these candidates are still lacking in terms of their intrinsic optoelectronic nature and predominant process of carrier dynamics, which precludes a rational design of various compositions, crystal structures, and device physics.

In the work presented in Chapter 5, the author performed a rigorous exploration of Bi- and Sb-based materials through the use of contact-less, time-resolved microwave conductivity (TRMC) measurements along with electrochemical characterizations.<sup>28</sup> TRMC measurements yield the transient photoconductivity ( $\Delta \sigma$ ), which provides an important factor associated with the intrinsic optoelectronics (eq. 1-5 in Chapter 1).<sup>29</sup> In addition, the TRMC measurements of multi-layered samples revealed the charge transfer from the active layer to the electron transport material (ETM) and hole transport material (HTM).<sup>30</sup> The author prepared a total of 44 different compositions, including 12 compositions of  $A_3M_2X_9$  (A = Cs, MA, FA, M = Bi, Sb, X = I, Br), 4 compositions of MSX (M = Bi, Sb, X = I, Br), 2 compositions each of  $M_2S_3$  and  $AgMI_4$  (M = Bi, Sb), 12 compositions of  $A_2MM'X_6$  DP (A = Cs, MA, FA, M = Bi, Sb, M' = Ag, X = I, Br), and 12 compositions of AMSX<sub>2</sub> SAP (A = Cs, MA, FA, M = Bi, Sb, X = I, Br) and characterized them by X-ray diffraction (XRD), UV-vis photoabsorption spectroscopy, and photoelectron yield spectroscopy (PYS). Based on the TRMC and solar cell characterizations, the combination of the active layer and chemical structure of the HTMs were found to significantly influence the charge extraction, rather than the energy-level matching of the conduction band minimum (CBM) and valence band maximum (VBM).

# 5-2. Results and Discussion

## 5-2-1. Structural characterization

Performing the initial characterization, XRD measurements were conducted on the 44 film samples (Figure 5-1) prepared by solution process (see Experimental). The XRD patterns of  $A_3M_2X_9$  were revealed to be consistent with the previous reports<sup>4,5,7</sup> or reconstructed XRD patterns of Crystallographic Open Database (COD) data, confirming the formation of the expected multi-crystalline films (Figure 5-1a, b, i, j, Table 5-1). They showed high crystallinities, as evident from the XRD peaks, which were much more intense than those of the other samples. It is assumed that the isolated  $[M_2X_9]^{3-}$  units with reduced crystal strain facilitate the growth of large crystal grains.

For the rod-like MSX structure, expected crystalline XRD profiles were obtained in BiSI, BiSBr, and SbSI films, whereas the SbSBr film exhibited no peaks (Figure 5-1c, k). Thus, this film was renamed as "Sb-S-Br". Of note, the annealing of SbSI at 240 °C revealed the appearance of Sb<sub>2</sub>S<sub>3</sub> contamination (Figure 5-1k). Energy dispersive X-ray fluorescence (EDX) measurements of the SbSI at 240 °C and Sb-S-Br films clearly showed the presence of expected elements (SbSI at 240 °C, Sb : S : I = 1.0 : 0.89 : 0.89; Sb-S-Br, Sb : S : Br = 1.0 : 0.42 : 1.5, Table 5-2).

The chalcogenide films (M<sub>2</sub>S<sub>3</sub>) were prepared by chemically assisted spin-coat and crystallization (CASC) process (Figure 5-1d, l), which yields a Bi<sub>2</sub>S<sub>3</sub> thin film with high electronic and morphological qualities as shown in chapter  $3^{31}$  exhibiting appropriate multi-crystalline films in both Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub>. Regarding silver bismuth/antimony iodide, AgBiI<sub>4</sub> showed the expected XRD patterns analogous to the CdCl<sub>2</sub> structure,<sup>11</sup> whereas AgSbI<sub>4</sub> did not. In the case of DPs (A<sub>2</sub>MM'X<sub>6</sub>), a significant contamination of A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> was observed in all their XRD peaks, except for Cs<sub>2</sub>AgBiBr<sub>6</sub> (Figure 5-1e, f, m, n). Despite the correct inclusion of each component in obtained film (Table 5-2) and their moderate Goldschmidt tolerance factors (0.88–1.09, Table 5-3),<sup>32,33</sup> the formation of A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> was dominant as the dimer and layered structures were thermodynamically more stable than that of the DPs.

For the SAPs (AMSX<sub>2</sub>), remnant contamination-originated XRD peaks arisen from  $A_3M_2X_9$  were also observed, except CsSbSI<sub>2</sub> and MASbSI<sub>2</sub> (Figure 5-1g, h, o, p). The XRD profiles of MASbSI<sub>2</sub> were identical to those reported by Nie *et al.*<sup>22</sup> Although the XRD references for the other SAP materials could not be found, the pattern of CsSbSI<sub>2</sub> is analogous to that of MASbSI<sub>2</sub>; thus, the CsSbSI<sub>2</sub> is assumed to be appropriately formed. Meanwhile, the other compositions failed to form SAP structure, resulting in the dominant formation of A<sub>3</sub>M<sub>2</sub>X<sub>9</sub>. Importantly, the author developed a simple one-step spin-coating

method using metal ethylxanthate<sup>34</sup> as the metal and sulfur source for the preparation of MSX and SAP thin films. This is completely different from the previously reported stepby-step chemical bath deposition (CBD) and spin-coating methods.<sup>22</sup> Accordingly, the author summarized the results of the XRD measurements and categorized them into four types: (A) well-identified without contamination, (B) includes a little contamination, (C) includes dominant contamination, and (U) crystal structures are unable to be resolved (Table 5-1). Hereafter, because large part of DP and SAP precursor yielded A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> structures, those samples are identified as "A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> from A<sub>2</sub>AgMX<sub>6</sub>/AMSX<sub>2</sub> precursor".



**Figure 5-1.** XRD patterns of all the samples. Contamination of other crystal phases such as  $A_3M_2X_9$  is given by the dots.

**Table 5-1.** Categorized class of crystal structures evaluated from XRD measurements. (A) without contamination, (B) including a little contamination, (C) including dominant contamination, and (U) crystal structures are unable to be resolved due to the lack of reference or amorphous nature.

Crystal	Precursor	Class	Reference <sup>a</sup>	Precursor	Class	Reference <sup>a</sup>
structure						
$A_3M_2X_9\\$	Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	А	COD:	$Cs_3Sb_2I_9$	А	COD:
			8103859			1537132
	MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	А	COD:	$MA_3Sb_2I_9 \\$	А	COD:
			4344961			7237225
	FA3Bi2I9	А	COD:	$FA_3Sb_2I_9$	А	Ref. 4
			7237621			
	$Cs_3Bi_2Br_9$	А	COD:	$Cs_3Sb_2Br_9$	А	COD:
			1531067			1537138
	MA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	А	Ref. 5	$MA_3Sb_2Br_9$	А	Ref. 7
	FA3Bi2Br9	А	COD:	$FA_3Sb_2Br_9$	А	-
			7701111			
MSX	BiSI	В	COD:	SbSI	А	COD:
			1535800			1535787
	BiSBr	А	COD:	SbSBr	U	COD:
			1535795			1521208
Layered	$Bi_2S_3$	А	COD:	$\mathbf{Sb}_2\mathbf{S}_3$	А	COD:
			9003473			1011154
	AgBiI <sub>4</sub>	А	Ref. 11	AgSbI <sub>4</sub>	U	-
DP	Cs <sub>2</sub> AgBiI <sub>6</sub>	С	-	$Cs_2AgSbI_6$	С	-
	MA <sub>2</sub> AgBiI <sub>6</sub>	С	-	MA <sub>2</sub> AgSbI <sub>6</sub>	С	-
	FA2AgBiI6	С	-	$FA_2AgSbI_6$	С	-
	Cs <sub>2</sub> AgBiBr <sub>6</sub>	А	COD:	$Cs_2AgSbBr_6$	В	Ref. 16
			4131244			
	MA2AgBiBr6	А	Ref. 15	MA <sub>2</sub> AgSbBr	С	
				6		
	FA2AgBiBr6	U	-	FA2AgSbBr6	С	-
SAP	CsBiSI <sub>2</sub>	С	-	CsSbSI <sub>2</sub>	U	-
	MABiSI <sub>2</sub>	С	-	MASbSI <sub>2</sub>	В	Ref. 22
	FABiSI <sub>2</sub>	С	-	FASbSI <sub>2</sub>	С	-
	$CsBiSBr_2$	С	-	$CsSbSBr_2$	С	-
	$MABiSBr_2$	С	-	MASbSBr <sub>2</sub>	С	-
	FABiSBr <sub>2</sub>	С	-	FASbSBr <sub>2</sub>	С	-

<sup>a</sup> Crystallography Open Database (COD) number or the reference number in the main text.

Precursor	Elemental ratio	Precursor	Elemental ratio
SbSI	Sb : S : I	CsBiSI <sub>2</sub>	Cs : Bi : S : I
(240 °C)	= 1.0 : 0.89 : 0.89		= 0.92 : 1.0 : 0.72 : 2.4
SbSBr	Sb : S : Br	MABiSI <sub>2</sub>	Bi : S : I = 1.0 : 0.46 : 2.2
(240 °C)	= 1.0 : 0.42 : 1.5		
Cs <sub>2</sub> AgBiI <sub>6</sub>	Cs : Ag : Bi : I	FABiSI <sub>2</sub>	Bi : S : I = 1.0 : 0.35 : 2.2
	= 1.6 : 0.97 : 1.0 : 4.8		
MA <sub>2</sub> AgBiI <sub>6</sub>	Ag : Bi : I	$CsBiSBr_2$	Cs : Bi : S : Br
	= 0.90 : 1.0 : 5.1		= 0.84 : 1.0 : 0.77 : 2.8
FA <sub>2</sub> AgBiI <sub>6</sub>	Ag: Bi: I = 0.93: 1.0:	$MABiSBr_2$	Bi : S : Br
	5.1		= 1.0 : 0.52 : 2.6
Cs <sub>2</sub> AgSbI <sub>6</sub>	Cs : Ag : Sb : I	FABiSBr <sub>2</sub>	Bi : S : Br
	= 2.0 : 0.98 : 1.0 : 5.0		= 1.0 : 0.54 : 2.5
MA <sub>2</sub> AgSbI <sub>6</sub>	Ag : Bi : I	$MASbSI_2$	Sb : S : I = 1.0 : 1.0 : 1.6
	= 0.94 : 1.0 : 5.3		
FA <sub>2</sub> AgSbI <sub>6</sub>	Ag : Bi : I	FASbSI <sub>2</sub>	Sb : S : I = 1.0 : 0.62 : 1.5
	= 0.98 : 1.0 : 5.4		
MA <sub>2</sub> AgSbBr	Ag : Bi : Br	FASbSBr <sub>2</sub>	Sb: S: Br
6	= 0.83 : 1.0 : 6.3		= 1.0: 0.77: 2.7
FA <sub>2</sub> AgSbBr <sub>6</sub>	Ag : Bi : Br		
	= 0.74 : 1.0 : 7.1		

**Table 5-2.** Summary of elemental analysis by EDX on the compositions which showed dominant formation of other crystal phase such as  $A_3M_2X_9$ . Note that MA and FA which is composed of C, N, and H cannot be detected.

Structure	Bi-based	Т	Sb-based	Т
-	Cs <sub>2</sub> AgBiI <sub>6</sub>	0.876	Cs <sub>2</sub> AgSbI <sub>6</sub>	0.914
	MA <sub>2</sub> AgBiI <sub>6</sub>	0.939	$MA_2AgSbI_6$	0.979
חת	FA2AgBiI6	1.02	FA <sub>2</sub> AgSbI <sub>6</sub>	1.06
DP	Cs <sub>2</sub> AgBiBr <sub>6</sub>	0.890	$Cs_2AgSbBr_6$	0.931
	MA <sub>2</sub> AgBiBr <sub>6</sub>	0.958	MA <sub>2</sub> AgSbBr <sub>6</sub>	1.00
	FA2AgBiBr6	1.04	FA2AgSbBr6	1.09
	$CsBiSI_2$	0.928	CsSbSI <sub>2</sub>	1.02
	MABiSI <sub>2</sub>	0.994	MASbSI <sub>2</sub>	1.08
SAD	$FABiSI_2$	1.08	$FASbSI_2$	1.18
SAP	CsBiSBr <sub>2</sub>	0.920	CsSbSBr <sub>2</sub>	1.01
	MABiSBr <sub>2</sub>	0.990	MASbSBr <sub>2</sub>	1.09
	FABiSBr <sub>2</sub>	1.08	FASbSBr <sub>2</sub>	1.18

**Table 5-3.** Summary of calculated Goldschmidt tolerance factors (*T*) of DPs and SAPs. The equation is followed;  $T = (r_A + r_X)/(2^{1/2}(r_B + r_X))$  where  $r_A$ ,  $r_B$ , and  $r_X$  are the effective ionic radii of A site, B site, and X site ion, respectively.<sup>32,33</sup>

#### 5-2-2. Energy level characterization

The energy levels of the VBM and CBM were measured using optical spectroscopy and PYS, as shown in Figure 5-2 (the original profiles are provided in Experimental). CBM levels were determined by adding the optical bandgaps (direct or indirect transition analysis based on the Tauc plots) to the VBM levels. The bandgap energies of the  $A_3M_2X_9$ materials were expectedly wide (2.1–2.8 eV), owing to their poor orbital overlaps of the [M<sub>2</sub>X<sub>9</sub>]<sup>3-</sup> units. Notably, Sb-based A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> materials have relatively shallower VBM (-5.5 to -6.1 eV) than Bi-based ones (-5.8 to -6.3 eV). This trend was also observed in other structures, suggesting that Sb-based materials fit the energy levels of common ETM/HTM more suitably than Bi-based ones do. SbSI, Sb-S-Br, Bi<sub>2</sub>S<sub>3</sub>, and Sb<sub>2</sub>S<sub>3</sub> exhibited moderate VBM levels (-5.5 to -5.6 eV) and bandgaps (1.4-1.8 eV). Although AgBiI<sub>4</sub> has a relatively narrow bandgap (1.8 eV), its deep VBM level is not ideal for energy-level matching with ETM/HTM. For the perovskite materials, DPs exhibited the wider bandgaps (2.2-2.9 eV) than SAPs (1.8-2.4 eV), as seen in the pictures of the films (Figure 5-3). Some SAPs, such as CsSbSI<sub>2</sub> and MASbSI<sub>2</sub>, demonstrate moderate VBM (-5.6 eV) and CBM levels (-3.7 eV), suitable for charge transfer to ETM/HTM and efficient light absorption.

From the standpoint of VBM level (> -5.7 eV) and bandgap (< 2.0 eV), the author expected Sb-based MSX materials (SbSI and Sb-S-Br), Bi- and Sb-based layered materials (Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub>), and Sb-based SAPs (CsSbSI<sub>2</sub> and MASbSI<sub>2</sub>) to be plausible candidates for use in efficient solar cells.



Figure 5-2. Energy levels of VBM and CBM for direct transition of the 44 Bi- and Sb-based films and MAPbI<sub>3</sub> obtained from PYS and UV-vis. TiO<sub>2</sub> and poly(tri-arylamine): PTAA are shown as the typical ETM and HTM. The compositions categorized as (C) (formation of different phase is dominant) in Table 5-1 are described with pale colored bar. The asterisk (\*) represents the data from Chapter 4.<sup>5</sup>



**Figure 5-3.** Pictures of Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, Cs<sub>3</sub>Sb<sub>2</sub>I<sub>9</sub>, AgBiI<sub>4</sub>, AgSbI<sub>4</sub>, Cs<sub>2</sub>AgBiBr<sub>6</sub>, Cs<sub>2</sub>AgSbBr<sub>6</sub>, SbSI (200 °C), SbSI (240 °C), double-coated SbSI (240 °C), Sb-S-Br (240 °C annealed), Sb<sub>2</sub>S<sub>3</sub>, and CsSbSI<sub>2</sub> films. The film thickness of active layer/mp-TiO<sub>2</sub> with a standard deviation is appended in brackets. The thickness of mp-TiO<sub>2</sub> is  $145 \pm 7$  nm.

#### 5-2-3. Photoconductivity and electron transport evaluation by TRMC

To evaluate the photoconductive properties of the Bi- and Sb-based materials, the author performed Xe-flash TRMC measurements using a pseudo-sunlight white light pulse as the excitation<sup>28</sup>. Figure 5-4 shows the maximum transient photoconductivity  $(\Delta\sigma_{max})$  of the active layer (single *i* layer drawn by narrow black bars) and mesoporous TiO<sub>2</sub> (mp-TiO<sub>2</sub>)/active layer (*n/i* double layer drawn by wide colored bars) (original TRMC decay are provided in Experimental). The  $\Delta\sigma_{max}$  value corresponds to the time-resolved peak of transient photoconductivity and provides a figure-of- merit that includes the generated charge carrier density, local charge carrier mobilities, charge carrier lifetimes at the end of the pulse (~10 µs), and the photoabsorption of the active layer. The single layers of Bi- and Sb-based materials, except for Bi<sub>2</sub>S<sub>3</sub>, showed a  $\Delta\sigma_{max}$  2–3 orders of magnitude lower than that of MAPbI<sub>3</sub> (Figure 5-4, narrow black bars), implying that the charge carrier mobilities of these materials are much smaller than that of MAPbI<sub>3</sub> (1–

100 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>30,35</sup> Although Bi<sub>2</sub>S<sub>3</sub> demonstrated high performance as a photodetector comparable to MAPbI<sub>3</sub>,<sup>31</sup> the *n*-doping in the darkness<sup>36</sup> lead decrease in  $R_{\rm sh}$  and inhibit an escalation in the PCE of the  $Bi_2S_3$ -based solar cell (<1%). Meanwhile, some materials, such as SbSI, Sb<sub>2</sub>S<sub>3</sub>, and MASbSI<sub>2</sub>, exhibit low  $\Delta \sigma_{max}$ , whereas their reported J<sub>SC</sub> values of solar cells under AM1.5G are relatively high, SbSI: 9.11 mA cm<sup>-2</sup> (FTO/compact-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/SbSI/HTM/Au), Sb<sub>2</sub>S<sub>3</sub>: 16.1 mA cm<sup>-2</sup> (FTO/compact-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/Au), and MASbSI<sub>2</sub>: 8.12 mA cm<sup>-2</sup> (FTO/compact-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/MASbSI<sub>2</sub>/ HTM/Au).<sup>19,22,27</sup> This inconsistency is resolved by focusing on the results of n/i double layers, in which SbSX, Sb<sub>2</sub>S<sub>3</sub>, AgSbI<sub>4</sub>, and Sb-SAPs showed a 10-fold increase in  $\Delta \sigma_{max}$ compared with those of the single layers (Figure 5-4, wide colored bars). This is attributed to the efficient electron transfer (ET) from the active layer to mp-TiO<sub>2</sub>, as observed in the mp-TiO<sub>2</sub>/Cs<sub>2</sub>AgBiBr<sub>6</sub> layer in Chapter 4.<sup>9</sup> The high  $\Delta \sigma_{\text{max}}$  of n/i double layer could be originated from holes remaining in the photoabsorber and/or electrons in mp-TiO<sub>2</sub>. Regardless of these two possibilities, the observed increase in  $\Delta \sigma_{max}$  suggests that (i) the electron mobilities in these Sb-based materials are lower than that in TiO<sub>2</sub> (~0.1  $cm^2V^{-1}s^{-1}$ ,<sup>37</sup> where the interdigitated mesoporous ETM structure benefits the high yield of the ET process and (ii) the charge carrier density at the pulse end is increased (=charge recombination is reduced by extracting electrons). Thus, the large  $\Delta \sigma_{\text{max}}$  of n/i double layer reflects efficient electron transport.

Based on the TRMC results of double layers and energetic assessments, the author expected the five most plausible materials to be SbSI, Sb-S-Br, Sb<sub>2</sub>S<sub>3</sub>, CsSbSI<sub>2</sub>, and MASbSI<sub>2</sub>, out of the 44 candidates. Interestingly, it was found that the ET was exceptionally efficient in a few Sb-based materials, despite the fact that other materials have CBM levels shallower than that of TiO<sub>2</sub>. This suggests that a favorable band bending may occur at TiO<sub>2</sub>/Sb-based materials interface or unfavorable energy barrier appears at TiO<sub>2</sub>/Bi-based materials interface.



Figure 5-4. Photoconductivity transient maxima ( $\Delta \sigma_{max}$ ) obtained from Xe-flash TRMC measurements. The narrow black bars and wide colored bars represent single active layer and mp-TiO<sub>2</sub>/active layer (n/i), respectively.

## 5-2-4. Statistical analysis of TRMC results and solar cell performance

*n-i-p* solar cells (glass/FTO/compact-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/HTM/Au, see Experimental) were fabricated and characterized for the materials that exhibited bandgaps smaller than 2.2 eV (for DP, smaller than 2.6 eV). The summary of a total of 29 materials are provided in Table 5-4. Among the devices using poly(tri-arylamine) (PTAA) with dopant as the HTM, Cs<sub>2</sub>AgBiBr<sub>6</sub> (DP) exhibited a relatively high PCE of 0.72% along with a low short-circuit current density ( $J_{SC}$ ) of 1.2 mA cm<sup>-2</sup>, high open-circuit voltage ( $V_{OC}$ ) of 0.93 V. However, the use of cychlopentadithiophene-benzothiadiazole copolymer (PCPDTBT) without dopant as HTM significantly suppressed its PCE to 0.3%, whereas CsSbSI<sub>2</sub>, Sb<sub>2</sub>S<sub>3</sub>, and SbSI (annealed at 240 °C) showed improvement in its PCE of 0.92%, 1.16%, and 1.35%, respectively, mainly owing to the increased  $J_{SC}$  (4.6–9.1 mA cm<sup>-2</sup>).



**Figure 5-5.** (a) Best PCE vs  $\Delta \sigma_{max}$  of double layer (mp-TiO<sub>2</sub>/active layer) obtained from Xe-flash TRMC. PTAA with dopant (triangles) and PCPDTBT without dopant (circles) were used as HTM. The color represents a crystal type as shown in Figure 5-2, 5-4. The dotted line is an eye-guide. (b)  $J_{SC}$  vs  $J_{SC}/J_{SC_max}$  and (c)  $J_{SC}$  vs  $J_{SC_max}$  plot obtained from the device results and calculation of  $J_{SC_max}$  (eq. 5-1). (d) Photon flux of AM1.5G sun light obtained from NREL.<sup>38</sup>

To examine the correlation between device performances and TRMC results, the best PCE of solar cells obtained using either PTAA or PCPDTBT as an HTM were plotted as a function of  $\Delta \sigma_{max}$  of n/i double layers (Figure 5-5a). A nearly linear correlation was observed with moderate correlation factor (r) of 0.59, demonstrating that TRMC measurements are useful for the exploration of Bi- and Sb-based photoabsorbers. AgSbI4, MASbSI2, and FASbSBr2 surrounded by dotted circles in Figure 5-5a are located far below the linear trend, which is presumably explained by inefficient hole transfer (HT) to HTM. The poor HT yield would be linked to the contamination of A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> phase for MASbSI2 and FASbSBr2 and the instability for AgSbI4 that easily turns transparent by exposing to the air for 1 h. Curiously, Cs<sub>2</sub>AgBiBr<sub>6</sub>, SbSI (annealed at 200 and 240 °C), and Sb-S-Br (annealed at 240 °C) devices showed a significant difference in PCE by changing HTM (for example, 0.16% for PTAA and 1.35% for PCPDTBT in the case of SbSI annealed at 240 °C, see Table 5-4). This indicates the importance of the selection of HTMs.

Because  $J_{SC}$  strongly predominate PCE (r = 0.93 for PCE vs  $J_{SC}$ , r = 0.43 for PCE vs  $V_{OC}$ , and r = 0.34 for PCE vs FF), the predominant factor of  $J_{SC}$  was studied through  $J_{SC}/J_{SC_{max}}$  analysis (Figure 5-5b, c), where  $J_{SC_{max}}$  is the achievable  $J_{SC}$  at maximum calculated from the integration of complementary transmittance and sunlight spectra (see Figure 5-5d). The calculation is as follows;

$$J_{\rm SC\_max} = -e \int_0^{\lambda a} P(\lambda) \{1 - T(\lambda)\} d\lambda$$
 (5-1)

, where *e* is the elemental charge,  $\lambda_a$  is the absorption edge,  $P(\lambda)$  is the photon flux of the solar spectrum, and  $T(\lambda)$  is the transmittance of mp-TiO<sub>2</sub>/photoabsorber double layer. The refection was ignored in this calculation. The  $J_{SC}$  vs  $J_{SC}/J_{SC}$ \_max plot showed a good linear correlation (r = 0.92), whereas the  $J_{SC}$  vs  $J_{SC}$ \_max plot was scattered (r = 0.31). Thus, the device performance is strongly affected by the efficiency of exciton separation and charge extraction rather than photoabsorption associated with the film thickness. Consequently, the author decided to focus on Sb<sub>2</sub>S<sub>3</sub>-containing SbSI annealed at 240 °C, which revealed the highest  $\Delta \sigma_{max}$  (except for MAPbI<sub>3</sub> and Bi<sub>2</sub>S<sub>3</sub>) and PCE, despite the fact that it remains mostly unexplored thus far.

	HTM: PTAA				HTM: PCPDTBT					
Materials	J <sub>SC</sub> (mA cm <sup>-2</sup> )	J <sub>SC</sub> / J <sub>SC_max</sub> <sup>a</sup>	V <sub>OC</sub> (V)	FF	PCE (%)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	$J_{SC_max}^{J_{SC}}/$	V <sub>OC</sub> (V)	FF	PCE (%)
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.082	0.0061	0.29	0.37	8.9×10 <sup>-3</sup>	0.41	0.030	0.48	0.49	0.098
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.12	0.0097	0.34	0.41	0.016	0.55	0.045	0.38	0.48	0.1
BiSI	0.19	0.0085	0.0024	0.085	4.0×10 <sup>-5</sup>	0.078	0.012	0.032	0.27	6.5×10 <sup>-4</sup>
BiSBr	0	0	0	0	0	0.36	0.037	0.003	0.16	2.0×10 <sup>-4</sup>
$Bi_2S_3$	0	0	0	0	0	0	0	0	0	0
AgBiI <sub>4</sub>	2.4	0.149	0.49	0.55	0.65	2.9	0.18	0.47	0.59	0.78
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from Cs <sub>2</sub> AgBiI <sub>6</sub> precursor	0.073	0.011	0.35	0.42	0.011	0.26	0.056	0.34	0.56	0.05
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from MA <sub>2</sub> AgBiI <sub>6</sub> precursor	0.24	0.035	0.48	0.5	0.057	0.48	0.070	0.39	0.65	0.12
FA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from FA <sub>2</sub> AgBiI <sub>6</sub> precursor	0.028	0.0041	0.13	0.38	1.4×10 <sup>-3</sup>	0.0051	0.0074	0.19	0.35	3.4×10 <sup>-3</sup>
$Cs_2AgBiBr_6$	1.2	0.22	0.95	0.67	0.76	1.1	0.20	0.46	0.59	0.31
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from CsBiSI <sub>2</sub> precursor	0.078	0.0074	0.032	0.27	6.5×10 <sup>-4</sup>	0.90	0.086	0.23	0.37	0.077
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from MABiSI <sub>2</sub> precursor	0.19	0.014	0.036	0.27	1.9×10 <sup>-3</sup>	0.29	0.020	0.012	0.22	7.6×10 <sup>-4</sup>
FA3Bi2I9 from FABiSI2 precursor	0.017	0.0019	0.11	0.36	7.1×10 <sup>-4</sup>	0.48	0.053	0.22	0.39	0.041
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from CsBiSBr <sub>2</sub> precursor	0.042	0.014	0.012	0.25	1.2×10 <sup>-4</sup>	0.6	0.19	0.062	0.27	0.01
MA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from MABiSBr <sub>2</sub> precursor	0.032	0.0025	0.0059	0.16	3.1×10 <sup>-5</sup>	0.83	0.065	0.017	0.23	3.2×10 <sup>-3</sup>
FA3Bi2Br9 from FABiSBr2 precursor	0.41	0.0018	0.14	0.34	0.019	0.022	0.033	0.1	0.36	8.1×10 <sup>-4</sup>
Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	0.14	0.020	0.24	0.6	0.021	0.62	0.086	0.37	0.44	0.1
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	0.18	0.039	0.32	0.49	0.028	0.46	0.099	0.29	0.54	0.074
SbSI (200 °C)	0.31	0.028	0.20	0.37	0.023	3.4	0.31	0.31	0.38	0.40
SbSI (240 °C)	0.67	0.051	0.42	0.56	0.16	7.1	0.57	0.37	0.53	1.35
Sb-S-Br (240 °C)	0.33	0.040	0.41	0.56	0.076	5.2	0.62	0.4	0.53	1.1
$\mathbf{Sb}_2\mathbf{S}_3$	6.1	0.35	0.41	0.39	0.98	9	0.51	0.29	0.44	1.16
AgSbI <sub>4</sub>	0.17	0.092	0.32	0.56	0.031	0.9	0.18	0.33	0.59	0.17

 Table 5-4. Summary of solar cell performances with various active layer.

Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from										
Cs2AgSbI6	0.15	0.039	0.34	0.46	0.023	0.62	0.16	0.25	0.56	0.087
precursor										
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from										
MA <sub>2</sub> AgSbI <sub>6</sub>	0.21	0.058	0.39	0.52	0.044	0.31	0.085	0.31	0.59	0.057
precursor										
$Cs_2AgSbBr_6$	0.29	0.061	0.46	0.5	0.068	0.53	0.11	0.37	0.45	0.088
CsSbSI <sub>2</sub>	1.5	0.022	0.43	0.47	0.31	4.6	0.025	0.38	0.53	0.92
0000012	1.0	0.022	0.10	0.17	0.01		0.020	0.20	0.00	0.72
MASbSI <sub>2</sub>	0.8	0.11	0.35	0.46	0.13	2.6	0.34	0.22	0.48	0.27
FA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from										
FASbSBr <sub>2</sub>	0.32	0.079	0.31	0.42	0.04	1.24	0.26	0.24	0.44	0.13
precursor										

<sup>a</sup>  $J_{SC_max}$  is the maximum  $J_{SC}$  calculated from the transmittance of mp-TiO<sub>2</sub>/active layer and sunlight spectrum, as represented in eq. 5-1.

## 5-2-5. The Effect of the HTM structures

A dramatic improvement in  $Sb_2S_3$ -containing SbSI solar cells by changing the HTM from PTAA (PCE = 0.16%) to PCPDTBT (PCE = 1.35%) underscores the importance of HTM selection. Therefore, the author examined polymeric HTM (PTAA with dopant, PCPDTBT, and regioregular poly(3-hexylthiophene): P3HT), molecular



**Figure 5-6.** (a) Chemical (or crystal) structures of HTMs (P3HT,<sup>30</sup> PTAA,<sup>30</sup> PCPDTBT,<sup>42</sup> FDT,<sup>39</sup> BTT-3,<sup>40</sup> Spiro-OMeTAD,<sup>30</sup> and CuSCN<sup>41</sup>) used for SbSI devices. The HOMO (or VBM) levels taken from the corresponding references are appended. (b)  $J_{SC}$ , (c)  $V_{OC}$ , (d) FF, and (e) PCE vs. HOMO (or VBM) level of each HTM. Dopants were added in PTAA and molecular HTM (Spiro-OMeTAD, FDT, and BTT-3). (f) Schematic of coordination from the thiophene unit of HTM to the Sb ion at the surface of the Sb-based photoabsorber.

HTM (2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene: Spiro-OMeTAD with dopant, FDT with dopant,<sup>39</sup> and BTT-3 with dopant<sup>40</sup>), and inorganic HTM (CuSCN<sup>41</sup>) (Figure 5-6a). The corresponding device performance is summarized in Table 5-5. To ensure the ohmic contact between the HTM and the Au electrode, a PEDOT:PSS layer was inserted between them (the device structure is drawn in Experimental; MoO<sub>3</sub>/Ag is an alternative, but unsuccessful), resulting in an improved PCE (from 1.35% to 1.81%) (Table 5-6).<sup>22</sup> Double-spin-coated SbSI was also found to slightly improve the PCE (2.01%).

 $J_{SC}$ ,  $V_{OC}$ , FF, and PCE vs. the highest occupied molecular orbital (HOMO) levels of the HTMs are displayed in Figure 5-6b–e, respectively. Notably, the HTMs including thiophene units (P3HT, PCPDTBT, FDT, and BTT-3 plotted by red circles) afforded the higher PCE than the others (PTAA, Spiro-OMeTAD, and CuSCN plotted by green circles), among which the best PCE of 2.01% ( $J_{SC} = 9.2 \text{ mA cm}^{-2}$ ,  $V_{OC} = 0.46 \text{ V}$ , and FF = 48%) was obtained for PCPDTBT. This result indicates that thiophene unit greatly enhanced the hole transport, while the impact of the HTM HOMO level was insignificant. The reason for the enhanced device characteristics is likely the coordination of the thiophene lone pair on the active layer surface, as suggested in the Sb<sub>2</sub>S<sub>3</sub>/PCPDTBT interface (Figure 5-6f).<sup>42</sup> Such a surface interaction would facilitate the hole transport to the HTM, leading to an increase in  $J_{SC}$  and  $V_{OC}$ . It is also notable that molecular HTMs (especially BTT-3) afforded relatively high  $V_{OC}$  (0.52–0.61 V), even without the PEDOT:PSS layer. This is likely because of the easy penetration of a single molecule into the SbSI layer preferable for efficient surface passivation. The introduction of the PEDOT:PSS layer further increases  $J_{SC}$ , whereas the  $V_{OC}$  was slightly decreased.

HTM	HOMO	$J_{ m SC}$	$V_{\rm OC}$	FF	PCE
_	(eV)	$(mA cm^{-2})$	(V)		(%)
PTAA	$-5.15^{30}$	2.4	0.24	0.60	0.63
P3HT	$-4.9^{30}$	6.3	0.40	0.48	1.2
PCPDTBT	$-5.3^{42}$	9.2	0.46	0.48	2.01
Spiro-	$-5.1^{30}$	4.8	0.30	0.46	0.65
OMeTAD					
FDT	$-5.16^{39}$	7.9	0.39	0.50	1.5
BTT-3	$-5.37^{40}$	7.9	0.48	0.45	1.7
CuSCN	$-5.3^{41}$	4.4	0.32	0.39	0.54

Table 5-5. Summary of Sb<sub>2</sub>S<sub>3</sub>-containing SbSI solar cells with various HTMs.

#### 5-2-6. Improvement of Sb<sub>2</sub>S<sub>3</sub>-containing SbSI solar cell

The critical issue to be addressed in the SbSI device is the large  $V_{OC}$  loss of 1.33 eV (Table 5-4) relative to its optical bandgap (1.73 eV). This can be attributed to the many pinholes observed in the image obtained by scanning electron microscopy (SEM) (Figure 5-7a); these pinholes cause the shortening of the diode circuit. Notably,  $V_{OC}$  was successfully improved by introducing the pre-deposition of a thin SbSI layer and double spin-coating (finally 200 nm in thickness) (Table 5-6 and Experimental). Consequently, a maximum PCE of 2.91% ( $J_{SC} = 12.0 \text{ mA cm}^{-2}$ ,  $V_{OC} = 0.47 \text{ V}$ , and FF = 52%) was obtained (Figure 5-7b, average PCE =  $2.4 \pm 0.5\%$ ) by using PCPDTBT as the HTM.

The external quantum efficiency (EQE) spectra was in good agreement with the photoabsorption spectra given by the complementary of the transmittance (Figure 5-7c). The maximum EQE was 59% at 390 nm, and the integrated  $J_{SC}$  over the EQE spectrum (10.2 mA cm<sup>-2</sup>) was consistent with the  $J_{SC}$  under one sun (10.3 mA cm<sup>-2</sup> for the corresponding cell). The PCE of Sb<sub>2</sub>S<sub>3</sub>-containing SbSI was mostly comparable to the



**Figure 5-7.** (a) SEM image of the Sb<sub>2</sub>S<sub>3</sub>-containing SbSI surface. (b) *J-V* curve of the best performing cell. The obtained parameters are appended. (c) EQE spectrum of a SbSI device. The inset is the photoabsorption spectrum of an Sb<sub>2</sub>S<sub>3</sub>-containing SbSI film (100-T%, *T* is transmittance). (d) Normalized PCE as a function of storage time under dried condition (~10%RH, solid line) and high humidity (40~60%RH, dot line) under room light.

3.05% reported by Nie *et al.*, where step-by-step deposition with CBD and spin-coating was used.<sup>19</sup> However, the author's SbSI film was prepared by a new, facile spin-coating of dimethyl sulfoxide (DMSO) solution of the ethylxanthate complex of Sb(EtXa)<sub>3</sub> and SbI<sub>3</sub> (3:4 in mol%) followed by thermal annealing. Additionally, the device showed good stability in dried air (~10%RH) and humid air (40~60%RH) and kept 86% and 72% of initial PCE for 16 days, respectively (Figures 5-7d). This chapter presented the demonstration of the effective screening of Pb-free solar cells under the guidance of TRMC and photoabsorption/photoelectron spectroscopies, among which the Sb<sub>2</sub>S<sub>3</sub>-containing SbSI with thiophene-containing HTM was identified as the most promising candidate.

Device structure <sup>a)</sup>	Mask size	$J_{ m SC}$	V <sub>OC</sub>	FF	PCE
	$(mm^2)$	$(mA cm^{-2})$	(V)		(%)
А	3.14	7.1	0.37	0.53	1.35
В	3.14	8.5	0.40	0.52	1.81
B, double spin-coat	9.00	9.2	0.46	0.48	2.01
B, pre-deposition	9.00	9.1	0.48	0.49	2.10
and double spin-coat					
B, pre-deposition	4.00	12.0	0.47	0.52	2.91
and double spin-coat					

Table 5-6. Summary of Sb<sub>2</sub>S<sub>3</sub>-containing SbSI/PCPDTBT-based device performance.

<sup>a)</sup>Device structure A: FTO/compact-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/SbSI/PCPDTBT/Au. Device structure B: FTO/compact-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/SbSI/PCPDTBT/PEDOT:PSS/Au. The detail of double spin-coat and pre-deposition are described in Experimental.

## 5-3. Conclusion

In conclusion, the author conducted a comprehensive survey on Bi and Sb-based semiconducting materials with 6 structural categories and 44 compositions, considering (XRD), bandgap (UV-vis), phase formation VBM (PYS), and crystal photoconductivity/charge transfer (TRMC). Consequently, the Sb-based MSX, Sb<sub>2</sub>S<sub>3</sub>, AgSbI<sub>4</sub>, and SAP showed higher solar cell performances than the others, as suggested from the 10-fold increase in  $\Delta \sigma_{max}$  of TRMC in the mp-TiO<sub>2</sub>/active layer compared with the single layer. The increased  $\Delta \sigma_{\text{max}}$  is understood from the efficient electron transfer to mp-TiO<sub>2</sub> and reduced charge recombination. Among the candidates, Sb<sub>2</sub>S<sub>3</sub>-containing SbSI prepared by a new method with the use of Sb(EtXa)<sub>3</sub> exhibited the top-level  $\Delta \sigma_{max}$ and PCE; thus, further device optimization (insertion of PEDOT:PSS, screening of HTM, and a repeat of active layer coating) was applied. Interestingly, the inclusion of a thiophene unit in the HTM, rather than the HOMO level, greatly impacted the PCE, leading to an improved PCE of 2.91%. Importantly, these results indicate that even if the charge carrier mobility of active layer is much lower than the typical LHP, efficient charge extraction and improvement of solar cell efficiency are possible by the rational combination of the active layer and HTM. These findings on the photoabsorber composition, the HTM structure, and the premiere indicator of  $\Delta \sigma_{\text{max}}$  of n/i double layer will help a further exploration and development of Pb-free solar cells.

# 5-4. Experimental

## 5-4-1. Preparation

#### Materials

CsI, MAI, FAI, CsBr, MABr, FABr, thiourea, and potassium ethylxanthate were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. BiI<sub>3</sub>, BiBr<sub>3</sub>, BiCl<sub>3</sub>, Bi(OAc)<sub>3</sub>, SbI<sub>3</sub>, SbBr<sub>3</sub>, SbCl<sub>3</sub>, Sb(OAc)<sub>3</sub>, AgI, and AgBr were bought from Sigma-Aldrich Co., Ltd. Super dehydrated grade DMSO were purchased from Wako Chemical Industries Ltd. All chemicals were used without further purification. Bi(OAc)<sub>3</sub>, Sb(OAc)<sub>3</sub>, and thiourea were used for the preparation of Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> film through CASC process. BiCl<sub>3</sub>, SbCl<sub>3</sub>, and potassium ethylxanthate were used for the synthesis of Bi(EtXa)<sub>3</sub> and Sb(EtXa)<sub>3</sub>. Other chemicals were used for the preparation of A<sub>3</sub>M<sub>2</sub>X<sub>9</sub>, MSX, AgMX<sub>4</sub>, DP and SAP films.

## Synthesis of Bi(EtXa)<sub>3</sub> and Sb(EtXa)<sub>3</sub>

Bi(EtXa)<sub>3</sub> was synthesized by the reported process.<sup>34</sup> For Sb(EtXa)<sub>3</sub> preparation, 912 mg SbCl<sub>3</sub> was dissolved in 8 mL methanol. Then, 12 mL potassium xanthate solution (1 M) was added to obtain pale yellow precipitation. After the removal of the upper solution, Sb(EtXa)<sub>3</sub> was extracted by chloroform from the precipitation. The extracted solution was evaporated to remove excess amount of chloroform before recrystallization. The recrystallization of Sb(EtXa)<sub>3</sub> were repeated 2 times to remove contamination. Finally, high purity Sb(EtXa)<sub>3</sub> yellow single crystal was obtained (99.99% metal basis, analyzed by EDX).

### Film preparation of A<sub>3</sub>M<sub>2</sub>X<sub>9</sub>, MSX, AgMX<sub>4</sub>, DPs and SAPs photoabsorbers

All the materials were dissolved in anhydrous DMSO. For  $A_3M_2X_9$ , AX and MX<sub>3</sub> were dissolved at 0.75 and 0.5 M, respectively. For MSX, MX<sub>3</sub> and M(EtXa)<sub>3</sub> were dissolved at 0.4 and 0.3 M, respectively. The solution was diluted with DMSO for double spin-coating (precursor : DMSO = 1 : 0.5) and pre-deposition (precursor : DMSO = 1 : 3). For AgMX<sub>4</sub>, AgX and MX<sub>3</sub> were dissolved at 0.5 M. For A<sub>2</sub>AgMX<sub>6</sub> (DPs), AX, AgX, and MX<sub>3</sub> were dissolved at 0.5, 0.25, and 0.25 M, respectively. For AMSX<sub>2</sub> (SAPs), AX, MX<sub>3</sub>, and M(EtXa)<sub>3</sub> were dissolved at 0.5, 0.25, and 0.25 M, respectively. For AMSX<sub>2</sub> (SAPs), AX, MX<sub>3</sub>, and M(EtXa)<sub>3</sub> were dissolved at 0.5, 0.25, and 0.25 M, respectively. Each solution was spin-coated onto a bare quartz or mp-TiO<sub>2</sub> at 2000 rpm for 30 s. The optimum annealing temperatures were 110 °C for A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> and AgMX<sub>4</sub>, 200–240 °C for MSX, 150 °C for DP except for Cs<sub>2</sub>AgBiBr<sub>6</sub> (250 °C for Cs<sub>2</sub>AgBiBr<sub>6</sub>), and 150 °C for SAP. The annealing time was 10 min for all. 5 vol% of HI aqueous solution (57 wt%) was added into the precursor
solution of A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, BiSI, A<sub>2</sub>AgBiI<sub>3</sub>, and AgBiI<sub>4</sub> to increase the solubility and to prevent lack of iodide. Whereas, HI addition to Sb-based materials resulted in deteriorated TRMC signal and device performance. All the procedure was carried out inside a grove box (O<sub>2</sub> < 0 ppm, H<sub>2</sub>O < 0 ppm).

#### 5-4-2. Fundamental characterization

## PYS, XRD, UV-vis, and EDX

The VBM levels were measured by PYS using a Bunko Keiki Corp. BIP-KV201 (accuracy:  $\pm 0.02$  eV, extraction voltage = 10 V) in a vacuum (<  $10^{-2}$  Pa). The film was prepared onto an F-doped SnO<sub>2</sub> (FTO) layer on a glass substrate, which was contacted through aluminum tape and an Au-coated electrode. The profiles are provided in Figure 5-8, 5-9. XRD was performed by using a Rigaku Corp. MiniFlex-600 instrument (Cu K $\alpha$  radiation:  $\lambda = 1.54$  Å) in the air at room temperature. The photoabsorption spectra were measured using a Jasco Corp. V-730. Tauc plots were also obtained from absorption spectra. The profiles are given in Figure 5-10, 5-11. EDX measurements of power samples



Figure 5-8. PYS spectra of each film. The samples were prepared on FTO substrates.

prepared by drop cast of precursor solution were performed using a Malvern-Panalytical Epsion 1. The film thickness was measured using a Bruker Dektak XT surface profiler.



Figure 5-9. PYS spectra of each film. The samples were prepared on FTO substrates.



**Figure 5-10.** Photoabsorption spectra of each film. The samples were prepared on quartz substrate.



**Figure 5-11.** Photoabsorption spectra of each film. The samples were prepared on quartz substrate.

### TRMC measurement

Thin films were prepared on quartz plates and mp-TiO<sub>2</sub>/quartz. The sample was set in a resonant cavity and probed by continuous microwave at ca. 9.1 GHz. A pseudo-sunlight, white light pulse (width ~10  $\mu$ s) from an in-house Xe-flash lamp was exposed to the sample, and the change in the microwave power reflected from the cavity was amplified by a field effect transistor amplifier, detected by a detector, and recorded by an oscilloscope. The photoconductivity transient  $\Delta \sigma$  was calculated by equation 1-5 as described in Chapter 1. All experiments were conducted at room temperature in air. The original decays are provided in Figure 5-12, 5-13.



**Figure 5-12.** Xe-flash TRMC decays of films on mp-TiO<sub>2</sub>/quartz and bare quartz. All the measurements were conducted in air.



**Figure 5-13.** Xe-flash TRMC decays of films on mp-TiO<sub>2</sub>/quartz and bare quartz. All the measurements were conducted in air.

#### 5-4-3. Device Fabrication

A fluorine-doped tin oxide (FTO) substrate was cleaned with detergent, isopropyl alcohol, and deionized water, and a compact TiO<sub>2</sub> layer was deposited onto the FTO by spray pyrolysis using a solution of titanium diisopropoxide bis(acetylacetonate) (Sigma Aldrich) in ethanol (1:40 v/v) at 450 °C. A 200 nm-thick mp-TiO<sub>2</sub> layer was deposited onto the compact TiO<sub>2</sub> layer by spin-coating (5000 rpm, 30 s) of a diluted TiO<sub>2</sub> paste (30 NR-D) in ethanol (paste/ethanol = 1:7 w/w), followed by annealing at 125 °C for 5–20 min and sintering at 500 °C for 20 min. A precursor solution was spin-coated onto the substrates and annealed. For double spin-coating of SbSI, the diluted precursor solution was spin-coated and annealed (150 °C, 2 min), followed by a second spin-coating and annealing (240 °C, 10 min). For the pre-deposition of thin SbSI, the diluted precursor solution was spin-coated (4000 rpm, 30 s), and annealed (240 °C, 10 min) before double spin-coating. The schematics of these process are represented in Figure 5-14. The HTM solution was prepared with following composition: 10 mg/mL PTAA toluene solution with Li-TFSI and 4-tert-butylpyridine (tBP) (PTAA : Li-TFSI : tBP = 1 : 0.15 : 1.4 for weight), 10 mg/mL P3HT and PCPDTBT o-dichlorobenzene solution without dopant, Spiro-OMeTAD (70 mM), FDT (100 M), and BTT-3 (30 mM) with Li-TFSI, FK209, and tBP (HTM : Li-TFSI : FK209 : tBP = 1 : 0.12 : 0.06 : 0.35 for weight), and CuSCN (150 mM) propylsulfide solution. P3HT, PCPDTBT, and CuSCN was spin-coated at 2000 rpm for 30 s, while the others were spin-coated at 4000 rpm for 30 s. Li-TFSI and tBP were not used for the AgBiI4 and AgSbI4 solar cells because of dopant-induced degradation. PTAA, P3HT, and PCPDTBT were annealed at 100 °C for 10 min. For optimized SbSI solar cell, PEDOT:PSS (Clevious AI 4083) mixed with DMF (PEDOT:PSS : DMF = 1 : 2) was spin-coated onto the HTM and annealed at 130 °C for 5 min. Finally, Au electrode was evaporated to form a thickness of 70 nm. The schematics of device structures and the statistics of device performance are provided in Figure 5-15, 5-16.



**Figure 5-14.** Schematic image of (a) double spin-coating and (b) pre-deposition of thin SbSI. The original precursor solution (SbI<sub>3</sub> 0.4 M, Sb(EtXa)<sub>3</sub> 0.3 M) was diluted with DMSO; (a) precursor : DMSO = 1 : 0.5, (b) precursor : DMSO = 1 : 3. The detail is as follows: (a) the diluted solution was spin-coated onto the substrate (2000 rpm, 30 s), followed by annealing (150  $^{\circ}$ C, 2 min). After cooling the substrate to room temperature, the precursor solution was spin-coated again (2000 rpm, 30 s), and annealed (240  $^{\circ}$ C, 10 min). (b) The diluted solution was spin-coated again in the same manner with the process (a).



**Figure 5-15.** (a) Device structure used for the initial screening. (b) Optimized device structure of Sb<sub>2</sub>S<sub>3</sub>-containing SbSI device.



**Figure 5-16.** The statistics of solar cell performance of (a) Bi- and (b) Sb-based materials, which are corresponding to Table 4. The optimized  $Sb_2S_3$ -containing SbSI (at 240 °C), prepared by pre-deposition and double spin-coating, are described with blue circles in (b). For each device structure, 5~9 cells were measured.

## 5-5. Reference

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### **Chapter6: Conclusion of this Dissertation**

In this dissertation, the author investigated the mechanism of molecular-induced transformation of LHPs and THPs and developed Bi- and Sb-based materials for optoelectronic application. The effect of oxygen exposure to THP and the detail of LCST behavior of LHP nanoparticles with the addition of CH<sub>3</sub>NH<sub>2</sub> were elucidated. Consequently, motivated by the toxicity and the low stability of these materials, various Bi- and Sb-based semiconducting materials were studied as an alternative. The conclusion of these works are as follows.

#### Chapter 2

The details of molecular-induced transformation of LHP and THP were elucidated. For THP, the effect of air exposure and SnF<sub>2</sub> addition on the electrochemical and optoelectronic properties were investigated. PYS revealed the rapid deepening of VBM level. Whereas, SnF<sub>2</sub> addition suppressed the initial trap formation in FASnI<sub>3</sub>. TRMC revealed the significant decrease of  $\phi\Sigma\mu$  for all the samples. The temporal increase of  $\phi\Sigma\mu$  in MASnI<sub>3</sub> is explained by the formation of MA<sub>2</sub>SnI<sub>6</sub> phase, which has higher mobility and deeper VBM. These results provide the insights into the kinetics of degradation and the compositional effect on optoelectronics.

For LHP, the anomalous LCST behavior was observed in MAPbBr<sub>3</sub> nanoparticle colloidal solution with the addition of CH<sub>3</sub>NH<sub>2</sub>. Based on the control experiment of solution composition, temperature-dependent UV-vis, and single crystal XRD analysis, the transformation mechanism was revealed. This LCST system suggests a new application of halide perovskites as thermoresponsive photonic materials.

#### Chapter 3

Considering the toxicity and limited stability of LHPs and THPs, the author focused on Bi<sub>2</sub>S<sub>3</sub> with extremely high photoconductivity. To obtain high quality thin film, CASC process consisting of facial spin-coating, prethermal annealing, and subsequent crystallization was developed. This process yielded a highly crystallized and pure Bi<sub>2</sub>S<sub>3</sub> thin film, with the increased  $\phi \Sigma \mu_{max}$  (1.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) value. Temperature-dependent TRMC and TPC revealed band-like transport property at room temperature. The CASC-Bi<sub>2</sub>S<sub>3</sub> photoresistor demonstrated much higher on/off ratio (~460) and detectivity (10<sup>11</sup> Jones) than other films prepared by reported process, indicating high applicability of CASC process for metal sulfide-based optoelectronic devices.

#### Chapter 4

Comparative study of Bi-based dimer (A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, A = Cs, MA, FA) and DP (Cs<sub>2</sub>AgBiBr<sub>6</sub>) were conducted by using TRMC. DP single layer showed a relatively high TRMC signal owing to the higher electron and hole mobility. The results of n/i and n/i/p layer of DP suggests more efficient electron transfer to TiO<sub>2</sub> and higher hole mobility than those of DMs. However, the electron and hole transfer to ETM and HTM were still insufficient, resulting in low current density (1.2 mA cm<sup>-2</sup>) and PCE (0.72%). This result suggested the requirement for searching other absorbers with higher charge transport property.

#### Chapter 5

The author conducted a comprehensive survey on 44 different compositions of Biand Sb-based solar absorbers, through the evaluation of crystal phase formation (XRD), bandgap (UV-vis), VBM (PYS), and charge transfer (TRMC). Importantly, Sb-based materials including SbSX, Sb<sub>2</sub>S<sub>3</sub>, and SAP showed efficient electron transfer to mp-TiO<sub>2</sub>. This result suggests the high possibility of Sb-based solar absorbers.  $J_{SC}$ - $J_{SC}$ -max analysis revealed that internal charge separation and transport property predominate the current density rather than photoabsorption. Consequently, Sb<sub>2</sub>S<sub>3</sub>-containing SbSI prepared by new solution process exhibited the highest  $\Delta \sigma_{max}$  and PCE among the candidates. The author also explored various HTMs for Sb<sub>2</sub>S<sub>3</sub>-containing SbSI, and found the inclusion of thiophene unit in HTM greatly impact the PCE. These findings provide the key strategy for further development of Bi- and Sb-based solar cells.

Thereafter, this study provides the insight into the mechanism of molecularinduced transformation of LHP and THP, and the optoelectronic properties of various Biand Sb-based semiconducting materials. The author hopes this study will contribute to the development of new application of LHP, the improvement of THP solar cells, and the exploration of Bi- and Sb-based solar absorbers.

# **List of Publications**

 Thermoresponsive Emission Switching via Lower Critical Solution Temperature Behavior of Organic-Inorganic Perovskite Nanoparticles
 Ryosuke Nishikubo, Norimitsu Tohnai, Ichiro Hisaki, and Akinori Saeki\*

Adv. Mater. 2017, 29 (23), 1700047.

2. Minute-Scale Degradation and Shift of Valence-Band Maxima of (CH<sub>3</sub>NH<sub>3</sub>)SnI<sub>3</sub> and HC(NH<sub>2</sub>)<sub>2</sub>SnI<sub>3</sub> Perovskites upon Air Exposure

Ryosuke Nishikubo, Naoki Ishida, Yukie Katsuki, Atsushi Wakamiya, and Akinori Saeki\*

J. Phys. Chem. C 2017, 121 (36), 19650–19656.

3. Solution-Processed  $Bi_2S_3$  Photoresistor Film To Mitigate a Trade-off between Morphology and Electronic Properties

Ryosuke Nishikubo and Akinori Saeki\*

J. Phys. Chem. Lett. 2018, 9 (18), 5392-5399.

4. Comparative Study of Charge Carrier Dynamics in Bismuth-based Dimer and Double Perovskites

**Ryosuke Nishikubo** and Akinori Saeki\* J. Photopolym. Sci. Technol. **2019**, *32* (5), 735–740.

5. Optoelectronic and Energy Level Exploration of Bismuth and Antimony-Based Materials for Lead-Free Solar Cells

**Ryosuke Nishikubo**, Hiroyuki Kanda, Inés García-Benito, Agustín Molina-Ontoria, Gianluca Pozzi, Abdullah M. Asiri, Mohammad Khaja Nazeeruddin\*, and Akinori Saeki\* *Chem. Mater.* **2020**, *32 (15)*, 6416–6424.

# **List of Supplementary Publications**

6. High-Performance Long-Term-Stable Dopant-Free Perovskite Solar Cells and Additive-Free Organic Solar Cells by Employing Newly Designed Multirole  $\pi$ -Conjugated Polymers

Kakaraparthi Kranthiraja, Kumarasamy Gunasekar, Hyunji Kim, An-Na Cho, Nam-Gyu Park, Seonha Kim, Bumjoon J. Kim, **Ryosuke Nishikubo**, Akinori Saeki\*, Myungkwan Song\*, and Sung-Ho Jin\*

Adv. Mater. 2017, 29 (23), 1700183.

7. Solvent-Coordinated Tin Halide Complexes as Purified Precursors for Tin-Based Perovskites

Masashi Ozaki, Yukie Katsuki, Jiewei Liu, Taketo Handa, **Ryosuke Nishikubo**, Shinya Yakumaru, Yoshifumi Hashikawa, Yasujiro Murata, Takashi Saito, Yuichi Shimakawa, Yoshihiko Kanemitsu, Akinori Saeki, and Atsushi Wakamiya\* *ACS Omega* **2017**, *2 (10)*, 7016–7021.

8. Accomplishment of Multifunctional  $\pi$ -Conjugated Polymers by Regulating the Degree of Side-Chain Fluorination for Efficient Dopant-Free Ambient-Stable Perovskite Solar Cells and Organic Solar Cells

Kakaraparthi Kranthiraja, Sang Ho Park, Hyunji Kim, Kumarasamy Gunasekar, Gibok Han, Bumjoon J. Kim, Chang Su Kim, Soohyun Kim, Hyunjung Lee\*, **Ryosuke Nishikubo**, Akinori Saeki\*, Sung-Ho Jin\*, and Myungkwan Song\* *ACS Appl. Mater. Interfaces* **2017**, *9 (41)*, 36053–36060.

9. Highly efficient air-stable/hysteresis-free flexible inverted-type planar perovskite and organic solar cells employing a small molecular organic hole transporting material Saripally Sudhaker Reddy, Sungmin Shin, Um Kanta Aryal, **Ryosuke Nishikubo**, Akinori Saeki\*, Myungkwan Song\*, and Sung-Ho Jin\* *Nano Energy* **2017**, *41*, 10–17.

10. Lithium-Ion Endohedral Fullerene (Li+@C60) Dopants in Stable Perovskite Solar Cells Induce Instant Doping and Anti-Oxidation
Il Jeon, Hiroshi Ueno, Seungju Seo, Kerttu Aitola, Ryosuke Nishikubo, Akinori Saeki, Hiroshi Okada, Gerrit Boschloo, Shigeo Maruyama, and Yutaka Matsuo\*
Angew. Chem. Int. Ed. 2018, 57 (17), 4607–4611.

Photon Upconversion through a Cascade Process of Two-Photon Absorption in CsPbBr<sub>3</sub> and Triplet–Triplet Annihilation in Porphyrin/Diphenylanthracene
 Shogo Izakura, Wenting Gu, **Ryosuke Nishikubo**, and Akinori Saeki\*
 J. Phys. Chem. C 2018, 122 (26), 14425–14433.

12. Anomalous Dielectric Behavior of a Pb/Sn Perovskite: Effect of Trapped Charges on Complex Photoconductivity

Kento Yamada, **Ryosuke Nishikubo**, Hikaru Oga, Yuhei Ogomi, Shuzi Hayase, Shohei Kanno, Yutaka Imamura, Masahiko Hada, and Akinori Saeki\* *ACS Photonics* **2018**, *5 (8)*, 3189–3197.

13. Lead-Free Solar Cells based on Tin Halide Perovskite Films with High Coverage and Improved Aggregation

Jiewei Liu, Masashi Ozaki, Shinya Yakumaru, Taketo Handa, Ryosuke Nishikubo, Yoshihiko Kanemitsu, Akinori Saeki, Yasujiro Murata, RichardMurdey, and Atsushi Wakamiya\*

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