Effects of Cl Addition to Sb-Doped Perovskite-Type CH$_3$NH$_3$PbI$_3$ Photovoltaic Devices

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Abstract: The effects of SbI$_3$, PbCl$_2$, and NH$_4$Cl addition to perovskite CH$_3$NH$_3$PbI$_3$ precursor solutions on photovoltaic properties were investigated. TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl)-based photovoltaic devices were fabricated by a spin-coating technique, and the microstructures of the devices were investigated by X-ray diffraction and scanning electron microscopy. Current density-voltage characteristics and incident photon-to-current conversion efficiencies were improved by a small amount of Sb- and Cl-doping, which resulted in improvement of the efficiencies of the devices. The structure analysis indicated formation of a homogeneous microstructure by NH$_4$Cl addition with SbI$_3$.

Keywords: microstructure; photoconversion; solar cell; perovskite; Sb; Cl; NH$_4$Cl; antimony

1. Introduction

Solar cells consisting of a CH$_3$NH$_3$PbI$_3$ compound with a perovskite structure have been widely studied recently [1–4] because of the high photoconversion efficiencies compared with ordinary organic solar cells [5–7]. Since a conversion efficiency reached 15% [8], higher efficiencies have been achieved for various device structures and processes [9–12], and the photoconversion efficiency increased up to ca. 20% [13–15].

The photovoltaic properties of the solar cells strongly depend on the crystal structures and the compositions of the perovskite compounds. Halogen atom doping, such as chlorine (Cl) or bromine (Br), at the iodine (I) sites in the perovskite compounds have been studied [16–19]. The doped Cl atoms would lengthen the diffusion length of excitons, which would result in the increase in efficiency [7,20]. In addition, studies on metal atom doping, such as tin (Sn) [21], antimony (Sb) [22], germanium (Ge) [23,24], thallium (Tl) [24], or indium (In) [24] at the lead (Pb) sites have been carried out. The wavelength ranges of optical absorption were expanded by the Sn or Tl-doping [21,24], and the conversion efficiencies were improved by Sb-doping to the perovskite phase [22]. A detailed search on the metal and halogen doping at the Pb and I sites is interesting for both Pb-free devices and the effects on photovoltaic properties.

The purpose of the present work is to investigate photovoltaic properties and microstructures of photovoltaic devices with perovskite-type CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) compounds, which were prepared by a simple spin-coating technique in air. Sb is a group 15 element, and is expected to work as an electronic donor at the sites of the group 14 element Pb [21]. Cl is also expected to increase the carrier diffusion length in the perovskite phase [7,20], and an improvement of the crystallinity and morphology of the perovskite films was expected by adding NH$_4$Cl [25,26]. Effects of SbI$_3$, PbI$_2$, and NH$_4$Cl addition using a mixture solution of perovskite compounds on the photovoltaic properties...
and microstructures were investigated by light-induced current density-voltage (J-V) characteristics, incident photon-to-current conversion efficiency (IPCE), scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS), optical microscopy (OM), and X-ray diffraction (XRD).

2. Materials and Methods

A schematic illustration for the fabrication of the present TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) photovoltaic cells is shown in Figure 1. The details of the fabrication process are described in the reported papers [8,19,27–30], except for SbI$_3$ [22]. F-doped tin oxide (FTO) substrates were cleaned using an ultrasonic bath with acetone and methanol, and dried under nitrogen gas. 0.15 M and 0.30 M TiO$_2$ precursor solution was prepared from titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, Tokyo, Japan, 0.055 mL and 0.11 mL) with 1-butanol (1 mL), and the 0.15 M TiO$_2$ precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s, and annealed at 125 °C for 5 min. Then, the 0.30 M TiO$_2$ precursor solution was spin-coated on the TiO$_2$ layer at 3000 rpm for 30 s, and annealed at 125 °C for 5 min. This process of 0.30 M solution was performed two times, and the FTO substrate was sintered at 500 °C for 30 min to form the compact TiO$_2$ layer. After that, TiO$_2$ paste was coated on the substrate by spin-coating at 5000 rpm for 30 s. For the mesoporous TiO$_2$ layer, the TiO$_2$ paste was prepared with TiO$_2$ powder (Nippon Aerosil, Tokyo, Japan, P-25) with poly(ethylene glycol) (Nacalai Tesque, Kyoto, Japan, PEG #20000) in ultrapure water. The solution was mixed with acetylacetone (Wako Pure Chemical Industries, Osaka, Japan, 10 µL) and triton X-100 (Sigma-Aldrich, Tokyo, Japan, 5 µL) for 30 min, and was left for 12 h to suppress the bubbles in the solution. The bubbles were removed by annealed at 120 °C for 5 min and then at 500 °C for 30 min to form the mesoporous TiO$_2$ layer [31,32]. For the preparation of the perovskite compounds, a solution of CH$_3$NH$_3$I (Showa Chemical Co., Ltd., Tokyo, Japan, 98.8 mg), PbI$_2$ (Sigma-Aldrich, Tokyo, Japan), NH$_4$Cl (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and SbI$_3$ (Sigma-Aldrich), with a desired mole ratio in γ-butyrolactone (Nacalai Tesque, 275 µL), and N,N-dimethylformamide (DMF, Nacalai Tesque, 225 µL) was mixed at 60 °C. Addition of the DMF to γ-butyrolactone and NH$_4$Cl to the perovskite phase would improve photovoltaic properties [25,26,33]. The detailed preparation compositions of TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells with different additives are listed in Table 1. The solution of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) was then introduced into the TiO$_2$ mesopores by a spin-coating method and annealed at 100 °C for 15 min. Then, a hole transport layer (HTL) was prepared by spin-coating. As the HTL, a solution of 2,2',7,7'-tetrakis[N,N-di(p-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, Wako Pure Chemical Industries, 36.1 mg) in chlorobenzene (Wako Pure Chemical Industries, 0.5 mL) was mixed with a solution of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, Tokyo Chemical Industry, Tokyo, Japan, 260 mg) in acetonitrile (Nacalai Tesque, 0.5 mL) for 12 h. The former solution with 4-tert-butylpyridine (Aldrich, 14.4 µL) was mixed with the Li-TFSI solution (8.8 µL) for 30 min at 70 °C. All procedures were carried out in ordinary air. Finally, gold (Au) metal contacts were evaporated as top electrodes. Layered structures of the present photovoltaic cells were denoted as FTO/TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl)/spiro-OMeTAD/Au, as shown in Figure 1.

The J-V characteristics of the photovoltaic cells were measured under illumination at 100 mW cm$^{-2}$ by using an AM 1.5 solar simulator (San-ei Electric, Osaka, Japan, XES-301S). The solar cells were illuminated through the side of the FTO substrates, and the illuminated area was 0.090 cm$^2$. The IPCE of the cells were also investigated (Enli Technology, Kaohsiung City, Taiwan, QE-R). The microstructures of the thin films were investigated by using an X-ray diffractometer (Bruker, Kanagawa, Japan, D2 PHASER), an optical microscope (Nikon, Tokyo, Japan, Eclipse E600) and a scanning electron microscope (Jeol, Tokyo, Japan, JSM-6010PLUS/LA) equipped with EDS.
Table 1. Preparation composition of TiO$_2$/CH$_3$NH$_3$Pb$_{1-x}$Sb$_x$I$_3$–yCl$_y$ cells with different additives.

<table>
<thead>
<tr>
<th>Preparation Composition</th>
<th>Amount of Additives</th>
</tr>
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<tbody>
<tr>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>None</td>
</tr>
<tr>
<td>CH$<em>3$NH$<em>3$Pb$</em>{0.97}$Sb$</em>{0.03}$I$_{1.03}$</td>
<td>SbI$_3$ (9.5 mg)</td>
</tr>
<tr>
<td>CH$<em>3$NH$<em>3$Pb$</em>{0.95}$Sb$</em>{0.05}$I$<em>{2.96}$Cl$</em>{0.04}$</td>
<td>SbI$_3$ (9.5 mg) + PbCl$_2$ (7 mg)</td>
</tr>
<tr>
<td>CH$<em>3$NH$<em>3$Pb$</em>{0.97}$Sb$</em>{0.03}$I$<em>{3.03}$Cl$</em>{0.30}$</td>
<td>SbI$_3$ (9.5 mg) + NH$_4$I (10 mg)</td>
</tr>
</tbody>
</table>

Figure 1. Schematic illustration for the fabrication of CH$_3$NH$_3$Pb$_{1-x}$Sb$_x$I$_3$–yCl$_y$ photovoltaic cells.

3. Results and Discussion

The J-V characteristics of the TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl)/spiro-OMeTAD photovoltaic cells under illumination are shown in Figure 2a, which indicates an effect of Sb and Cl addition to the CH$_3$NH$_3$PbI$_3$. The measured photovoltaic parameters of TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells are summarized in Table 2. The CH$_3$NH$_3$PbI$_3$ cell provided a power conversion efficiency ($\eta$) of 7.05%, and the averaged efficiency ($\eta_{\text{ave}}$) of three electrodes on the cells is 6.66%, as listed in Table 2. A short-circuit current density ($J_{SC}$) increased up to 20.9 mA cm$^{-2}$ by an addition of SbI$_3$, which would indicate an increase of carrier concentration. The highest efficiency was obtained for a cell added with SbI$_3$ + NH$_4$I-Cl, which provided an $\eta$ of 9.71%, a fill factor (FF) of 0.579, a short-circuit current density ($J_{SC}$) of 19.6 mA cm$^{-2}$, and an open-circuit voltage ($V_{OC}$) of 0.843 V. An increase of photocurrent for the (SbI$_3$ + NH$_4$I-Cl)-added sample is observed at ~0.2 V in Figure 2a. Since a small amount of carriers might be generated and charged in the TiO$_2$ layer during J-V measurements under light irradiation and current flow, the electrical resistance would be reduced, and the photocurrent would increase. After 28 days, a decrease in the efficiencies of the cells were within 50%, except for the PbCl$_2$ addition, as shown in Figure 2b and Table 2. Efficiency decay rates are also listed in Table 2, which indicates the NH$_4$I Cl additives would be effective for device stability. Although the $J_{SC}$ values were almost preserved after 28 days, the fill factors decreased. The black color of the perovskite phase became light brown after 28 days, which would indicate the degradation of the crystal structure of the perovskite phase.

IPCE spectra of the CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells are shown in Figure 3. The perovskite CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) shows photoconversion efficiencies between 300 nm and 800 nm, which almost agrees with reported energy gaps of 1.51 eV [34] and 1.61 eV [35] (corresponding to 821 nm and 770 nm, respectively) for CH$_3$NH$_3$PbI$_3$. The IPCE was improved in the range of 450–750 nm by adding a small amount of Sb and Cl. In the present work, the energy gaps of the CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) phase were almost constant of 1.55 eV even by the Sb- and Cl-doping, which corresponded well to the constant values of the open-circuit voltages.
XRD patterns of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells on the FTO/TiO$_2$ are shown in Figure 4. The diffraction peaks can be indexed by a cubic crystal system (Pm3m) for the CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) thin films. Although the deposited films are a single perovskite structure, broader diffraction peaks due to the PbI$_2$ compound appeared in the CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) film, as shown in Figure 4. The Sb addition suppressed the formation of PbI$_2$ [22].

The CH$_3$NH$_3$PbI$_3$ crystals have perovskite structures, and both CH$_3$NH$_3$ ions and I ions are disordered, which results in the disordered cubic structure [22], as shown in Figure 5. For the as-deposited CH$_3$NH$_3$PbI$_3$ thin film, only XRD peaks of CH$_3$NH$_3$PbI$_3$ were observed, and no XRD peak of PbI$_2$ was observed [27]. After annealing at 100 °C for 15 min, the unit cell volume decreased and an XRD peak of PbI$_2$ appeared [27], which indicated partial separation of PbI$_2$ from CH$_3$NH$_3$PbI$_3$. The XRD result of CH$_3$NH$_3$PbI$_3$ in Figure 4 also showed the existence of PbI$_2$ after annealing at 100 °C for 15 min. This would indicate partial separation of PbI$_2$ from CH$_3$NH$_3$PbI$_3$ after annealing.

**Figure 2.** (a) J-V characteristic of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) photovoltaic cells; (b) J-V characteristic after 28 days.
would be an effect of SbI$_3$ with PbCl$_2$ in addition to the doping effect of Sb and Cl at the Pb and I sites, respectively. It is believed that these surface structures would affect the photovoltaic properties, as shown in Figure 6d, and few crystals with a special shape are observed. Perovskite crystals with sizes of ~10 µm are observed, and the crystals have a square-like shape. A completely different type of surface structure is observed for the CH$_3$NH$_3$Pb(Sb)I$_3$ cells added with SbI$_3$, as shown in Figure 6b. Perovskite crystals with sizes of ~10 µm are observed, and the crystals have a round shape, which would be an effect of SbI$_3$ addition. The sizes of round-shaped crystals increased up to ~20 µm by an addition of SbI$_3$ + PbCl$_2$, as shown in Figure 6c. By adding SbI$_3$ with NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$, the surface morphology was drastically changed, as shown in Figure 6d, and few crystals with a special shape are observed. It is believed that these surface structures would affect the photovoltaic properties, in addition to the doping effect of Sb and Cl at the Pb and I sites, respectively.

Table 2. Measured photovoltaic parameters (average and top) of TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells.

<table>
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<tr>
<th>Additive</th>
<th>J$_{SC}$ (mA cm$^{-2}$)</th>
<th>V$_{OC}$ (V)</th>
<th>FF</th>
<th>H (%)</th>
<th>$\eta_{ave}$ (%)</th>
<th>Decay Rate (%/Week)</th>
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<tr>
<td>None</td>
<td>16.8</td>
<td>0.870</td>
<td>0.482</td>
<td>7.05</td>
<td>6.66</td>
<td>-</td>
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<tr>
<td>SbI$_3$</td>
<td>20.9</td>
<td>0.877</td>
<td>0.386</td>
<td>7.08</td>
<td>6.57</td>
<td>-</td>
</tr>
<tr>
<td>SbI$_3$ + PbCl$_2$</td>
<td>16.7</td>
<td>0.888</td>
<td>0.551</td>
<td>8.17</td>
<td>7.51</td>
<td>-</td>
</tr>
<tr>
<td>SbI$_3$ + NH$_4$Cl</td>
<td>19.6</td>
<td>0.856</td>
<td>0.579</td>
<td>9.71</td>
<td>9.02</td>
<td>-</td>
</tr>
<tr>
<td>After 28 days</td>
<td>None</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SbI$_3$</td>
<td>17.3</td>
<td>0.739</td>
<td>0.390</td>
<td>4.98</td>
<td>4.56</td>
</tr>
<tr>
<td></td>
<td>SbI$_3$ + PbCl$_2$</td>
<td>16.6</td>
<td>0.782</td>
<td>0.332</td>
<td>4.31</td>
<td>4.02</td>
</tr>
<tr>
<td></td>
<td>SbI$_3$ + NH$_4$Cl</td>
<td>13.1</td>
<td>0.570</td>
<td>0.402</td>
<td>3.00</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>SbI$_3$ + NH$_4$Cl</td>
<td>16.0</td>
<td>0.787</td>
<td>0.438</td>
<td>5.51</td>
<td>4.99</td>
</tr>
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Figure 3. IPCE (incident photon-to-current conversion efficiency) spectra of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells.

Optical microscope images of CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) added with SbI$_3$, SbI$_3$ with PbCl$_2$, and SbI$_3$ with NH$_4$Cl photovoltaic cells are shown in Figure 6a–d, respectively. Perovskite crystals with sizes of 5–10 µm are observed at the surface of the mesoporous TiO$_2$, as shown in Figure 6a, and the crystals have a square-like shape. A completely different type of surface structure is observed for the CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells added with SbI$_3$, as shown in Figure 6b. Perovskite crystals with sizes of ~10 µm are observed, and the crystals have a round shape, which would be an effect of SbI$_3$ addition. The sizes of round-shaped crystals increased up to ~20 µm by an addition of SbI$_3$ + PbCl$_2$, as shown in Figure 6c. By adding SbI$_3$ with NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$, the surface morphology was drastically changed, as shown in Figure 6d, and few crystals with a special shape are observed. It is believed that these surface structures would affect the photovoltaic properties, in addition to the doping effect of Sb and Cl at the Pb and I sites, respectively.
Figure 4. XRD patterns of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells.

Figure 5. Structure model of cubic CH$_3$NH$_3$Pb(Sb)I$_3$(Cl).

Figure 7a is a SEM image of TiO$_2$/CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cell with an additive of SbI$_3$, which corresponds to the OM image of Figure 6b. The particle sizes are $\sim$10 $\mu$m, which agrees well with those observed in the OM image of Figure 6b. Elemental mapping images of Pb, Sb, I, C, and N by SEM-EDX are shown in Figure 7b–f, respectively. The elemental mapping images indicate the particles observed in Figure 7a correspond to the CH$_3$NH$_3$PbI$_3$ phase. The composition ratio of metal elements Pb, Sb, I, and C:N were calculated from the EDX spectrum using background correction by normalizing the spectrum peaks on the atomic concentration, as listed in Table 3. This result indicates that I might be deficient from the starting composition of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl), and the deficient I might increase
the hole concentration. In addition, carbon atoms are dispersed in the matrix, as shown in Figure 7e, which might be from γ-butyrolactone with a higher boiling point compared with that of DMF.

A SEM image of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cell with additives of SbI$_3$ with PbCl$_2$ is shown in Figure 8a. The particle sizes are 10–20 µm, which corresponds to those observed in the OM image of Figure 6c. Figure 8b–g are elemental mapping images of Pb M line, Sb L line, I L line, C K line, N K line, and Cl K line, respectively, which indicate the particles observed in Figure 8a correspond to the CH$_3$NH$_3$PbI$_3$ phase. The composition ratio of metal elements and C:N were calculated from the EDX spectrum, as listed in Table 3, which indicates that I might be deficient from the starting composition of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl). In Figure 8e, carbon atoms are also dispersed in the matrix, which is similar to the observed image of Figure 7e.

![Figure 6. Optical microscope images of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cells. The additives are (a) none; (b) SbI$_3$; (c) SbI$_3$ with PbCl$_2$; and (d) SbI$_3$ with NH$_4$Cl, respectively.](image)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Pb (%)</th>
<th>Sb (%)</th>
<th>I (%)</th>
<th>Cl (%)</th>
<th>C:N</th>
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<tr>
<td>SbI$_3$</td>
<td>33.7</td>
<td>BDL</td>
<td>66.3</td>
<td>-</td>
<td>60.5:39.5</td>
</tr>
<tr>
<td>SbI$_3$ + PbCl$_2$</td>
<td>30.5</td>
<td>BDL</td>
<td>67.5</td>
<td>2.0</td>
<td>58.4:41.6</td>
</tr>
<tr>
<td>SbI$_3$ + NH$_4$Cl</td>
<td>31.3</td>
<td>0.2</td>
<td>67.3</td>
<td>1.2</td>
<td>61.3:38.7</td>
</tr>
</tbody>
</table>
Figure 7. (a) SEM image of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cell with an additive of SbI$_3$; Elemental mapping images of (b) Pb M line, (c) Sb L line, (d) I L line, (e) C K line, and (f) N K line.

Figure 9a is a SEM image of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cell with additives of SbI$_3$ with NH$_4$Cl. By adding SbI$_3$ with NH$_4$Cl to the CH$_3$NH$_3$PbI$_3$, the surface morphology was drastically changed, and no special crystal shape is observed, which agrees well with the result of the OM image in Figure 6d. Elemental mapping images of Pb M line, Sb L line, I L line, C K line, N K line, and Cl K line are shown in Figure 9b–g, respectively. The images indicate the perovskite CH$_3$NH$_3$PbI$_3$ phase is dispersed homogeneously on the photovoltaic device. The composition ratio of metal elements and C:N were calculated from the EDX spectrum, as listed in Table 3, which indicates that no major difference is observed compared with the other devices. This suggests that the homogeneous surface structures would improve the photovoltaic properties, in addition to the doping effect of Sb and Cl at the Pb and I sites, respectively. From the SEM-EDX result, site occupancies of I atom would also be less than 1, which might be due to the partial separation of PbI$_2$ from the CH$_3$NH$_3$PbI$_3$ phase.
Figure 8. (a) SEM image of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cell with additives of SbI$_3$ with PbCl$_2$; Elemental mapping images of (b) Pb M line, (c) Sb L line, (d) I L line, (e) C K line, (f) N K line, and (g) Cl K line.
Figure 9. (a) SEM image of CH$_3$NH$_3$Pb(Sb)I$_3$(Cl) cell with additives of SbI$_3$ with NH$_4$Cl; Elemental mapping images of (b) Pb M line, (c) Sb L line, (d) I L line, (e) C K line, (f) N K line, and (g) Cl K line.
Three assumed mechanisms could be considered for the increase of the photoconversion efficiencies. The first mechanism is as follows: I⁻ ions would be attracted at the I sites by Sb³⁺ with more ionic valence compared with that of Pb²⁺, which resulted in the suppression of PbI₂ elimination from CH₃NH₃PbI₃. The suppression of PbI₂ would improve the TiO₂/CH₃NH₃PbI₃ interfacial structure, which also would improve the VOC values. As the amount of the Sb addition increase, the lattice constants would be decreased by an effect of Sb with a smaller ionic size compared with Pb.

The second mechanism is as follows: when a small amount of Cl was doped in the CH₃NH₃PbI₃ phase, diffusion length of excitons would be lengthened by the doped Cl atoms [7,20], which would also contribute to the JSC values. Further studies are needed for precise structure determination of the perovskite structure.

Although the device performance may not be perfectly optimized, the reproducibility of efficiency increases by elemental doping, such as with Cl or Sb, were confirmed in the present and previously reported works [7,20,22,25]. Therefore, it is believed that the addition of dopants, such as Cl or Sb, to the perovskite phase would be effective for the development of device performance. The effect of the Cl-doping without Sb-doping was not investigated in the present work, and further studies are needed.

An energy level diagram of TiO₂/CH₃NH₃Pb(Sb)I₃(Cl) photovoltaic cells is summarized as shown in Figure 10. The electronic charge generation is caused by light irradiation from the FTO substrate side. The TiO₂ layer receives the electrons from the CH₃NH₃Pb(Sb)I₃(Cl) crystal, and the electrons are transported to the FTO. The holes are transported to an Au electrode through spiro-OMeTAD. In the present work, the samples were prepared in air, which may result in the reduction of the stability. Perovskite crystals with higher quality should be prepared in further works.

**Figure 10.** Energy level diagram of CH₃NH₃Pb(Sb)I₃(Cl) cells.

### 4. Conclusions

Effects of SbI₃, PbCl₂, and NH₄Cl addition to perovskite CH₃NH₃PbI₃ precursor solutions on photovoltaic properties were investigated. TiO₂/CH₃NH₃Pb(Sb)I₃(Cl)-based photovoltaic devices were fabricated, and the microstructures of the devices were investigated by XRD, OM, and SEM-EDS.
J–V characteristics and IPCE were improved by a small amount of Sb- and Cl-doping. The structural analysis also indicated the formation of a homogeneous microstructure by SbI$_3$ addition with NH$_4$Cl, which improved the FF values and photoconversion efficiencies.

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**Author Contributions:** Takeo Oku wrote the manuscript and summarized the project. Yuya Ohishi fabricated and characterized the solar cells, and summarized the results. Atsushi Suzuki and Yuzuru Miyazawa supported the project.

**Conflicts of Interest:** The authors declare no conflict of interest.

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