Effects of guanidinium addition to CH$_3$NH$_3$PbI$_{3–x}$Cl$_x$ perovskite photovoltaic devices

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CH$_3$NH$_3$PbI$_{3–x}$Cl$_x$-based photovoltaic devices with guanidinium [C(NH$_2$)$_3$, GA] were fabricated and characterized. The additive effects of guanidinium iodide, formamidinium [CH(NH$_2$)$_2$, FA] iodide, and guanidinium chloride were compared. Short-circuit current densities, open-circuit voltages, series resistances and shunt resistances were improved by the GA addition. The short-circuit current densities were increased by FA addition with GA. The incident photon-to-current conversion efficiency increased, which results from the suppression of pin-holes in perovskite layers by GA addition. The conversion efficiencies were improved by GA addition. X-ray diffraction showed that the lattice constants of the perovskite crystals increased by GA and FA addition, and that the GA substituted partially at the CH$_3$NH$_3$-site.

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1. Introduction

Recently, thin-film solar cells with perovskite-type methylammonium trihalogenoplumbates (II) (CH$_3$NH$_3$PbI$_3$) compounds have been studied extensively because of their easy fabrication and high conversion efficiencies compared with conventional organic solar cells. Since a conversion efficiency of 15% was attained, higher efficiencies have been accomplished for various perovskite compounds and device structures, and conversion efficiencies above 20% have been achieved.

To estimate the structural stability of the perovskite crystal with ABX$_3$ structures, an empirical index, which is the Goldschmidt’s tolerance factor has been used commonly. This tolerance factor ($t$) is given by $t = (R_A + R_X)/\sqrt{2(R_B + R_X)}$ where $R_A$, $R_B$, and $R_X$ are the ionic radii of the A, B, and X ions in the ABX$_3$ perovskite structure, respectively. If $t$ is equal to 1, the perovskite crystals have ideal cubic structures.

It has been reported that the photovoltaic properties of perovskite solar cells depend strongly on the compositions and crystal structures of the perovskite compounds. Doping with metal atoms, such as tin (Sn), antimony (Sb), copper (Cu), cobalt (Co), arsenic (As), germanium (Ge), indium (In), or thallium (TI) at the lead (Pb) sites has been performed. The optical absorption ranges of the perovskite compounds have been expanded by Sn or TI doping, and the photovoltaic conversion efficiencies of perovskite solar cells have been improved by Sb, Cu, Co or As doping. Doping with other elements, such as cesium, rubidium, formamidinium [CH(NH$_2$)$_2$, FA] or guanidinium [C(NH$_2$)$_3$, GA] at the methylammonium (CH$_3$NH$_3$, MA) sites has also improved the conversion efficiencies.

Studies on doping with halogen atoms, such as chlorine (Cl) or bromine (Br) at the iodine (I) sites of the perovskite crystals have also been reported. The doped Cl ions lengthened the diffusion length of excitons, which improved the conversion efficiency. Further studies on metal, halogen, and/or FA doping at the Pb, I and/or MA sites are fascinating because of their effects on the photovoltaic properties and microstructures of the perovskite solar cells. Microstructure control of the perovskites by using polylines and other polymers has improved the performance effectively.

The purpose of this work was to investigate the effects of guanidinium-iodide (GAI), guanidinium-chloride (GACl), and formamidinium-iodide (FAI) addition to CH$_3$NH$_3$PbI$_{3–x}$Cl$_x$-based perovskite. GA addition is expected to extend the carrier life time and to reduce the carrier recombination in the perovskite layers. GACl addition is expected to provide effects of GA and Cl additions. FA addition is expected to expand the wavelength range of light adsorption. The effects of these additives on the formation of perovskite compounds for the photovoltaic cells were investigated by light-induced current-density–voltage ($J–V$) characteristics, the incident photon-to-current conversion efficiency (IPCE), X-ray diffractometry (XRD), optical microscopy, and scanning-electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS).
2. Experimental procedures

A schematic illustration of the fabrication of the perovskite photovoltaic cells is shown in Fig. 1. Details of the basic fabrication are described in published reports. F-doped tin-oxide (FTO) substrates were cleaned by using an ultrasonic bath with acetone and methanol, and dried under nitrogen. TiO2 precursor solutions (0.15 and 0.30 M) were prepared from titanium diisopropoxide bis(acetyl-acetonate) (Sigma-Aldrich, 0.055 and 0.11 mL) with 1-butanol (1 mL), and the 0.15 M TiO2 precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s and heated at 125°C for 5 min in air to form a TiO2 layer. The 0.30 M TiO2 precursor solution was spin-coated onto the TiO2 layer at 3000 rpm for 30 s, and heated at 125°C for 5 min. The process of coating with a 0.30 M solution was performed two times, and the FTO substrate was annealed at 550°C for 30 min to form a compact TiO2 layer. For the mesoporous TiO2 layer, TiO2 paste was prepared with TiO2 powder (Nippon Aerosil, P-25) with poly(ethylene glycol) (Nacalai Tesque, PEG #20000) in ultrapure water. The solution was mixed with acetylacetone (Wako Pure Chemical Industries, 10 μL) and triton X-100 (Sigma-Aldrich, 5 μL) for 30 min, and left for 12 h to suppress the bubbles in the solution. The TiO2 paste was coated onto the substrate by spin-coating at 5000 rpm for 30 s. The cells were annealed at 120°C for 5 min and at 550°C for 30 min to form a mesoporous TiO2 layer.

To prepare the perovskite compounds, a solution of CH3NH3I (Showa Chemical Co. Ltd., 190.7 mg) and PbCl2 (Sigma-Aldrich, 111.2 mg) was prepared with a mole ratio of 3:1 in N,N-dimethylformamide (Nacalai Tesque, 500 μL) with additives of GAI (10 mol %, 7.5 mg), GACI (10 mol %, 3.8 mg), and GA+FAI+GACI, respectively. The reaction mechanism proposed for the CH3NH3PbI3 perovskite is: 3CH3NH3I + PbCl2 → CH3NH3PbI3 + 2CH3NH3Cl. Because 2CH3NH3Cl is generated as a byproduct during the reaction, the quantity 10 mol % means 10 mol % of produced CH3NH3PbI3. The solutions were stirred at 70°C for 24 h. Solutions of CH3NH3PbI3(Cl) were introduced into the TiO2 mesopores by spin coating and annealed at 150°C for 20 min (perovskite with additive) or 140°C for 15 min (standard) to form the perovskite layer. A hole transport layer was prepared by spin-coating onto the perovskite layer. For the hole transport layer, a solution of 2,2′,7,7′-tetrakis[N,N-dimethoxyphenyl]amino]-9,9′-spirobifluorene (spiro-OMeTAD, Wako Pure Chemical Industries, 36.1 mg) was mixed with a chlorobenzene solution of 0.5 mL, and a solution of lithium bis(trifluoromethanesulfonyle)imide (Li-TFSI, Tokyo Chemical Industry, 260 mg) were prepared and stirred 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. A hole transport layer was then prepared by spin-coating onto the perovskite layer. All procedures for preparation of the thin films were performed in ambient air. Finally, a gold (Au) thin films was evaporated onto the hole transport layer, as top metal electrodes. The layered structures of the solar cells were denoted FTO/TiO2/perovskite/spiro-OMeTAD/Au, as shown in Fig. 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-ai Electric, XES-301S). The J–V measurements were performed by using a source-measure unit (Keysight, B2901A Precision SMU). The scan rate and sampling time were ~0.08 V s–1 and 1 ms, respectively. Four cells were tested for each condition. The solar cells were illuminated through the sides of the FTO substrates, and the illuminated area was 0.090 cm2. The IPCE of the cells was also measured (Enli Technology, QE-R). The microstructures of the cells were investigated by using an X-ray diffractometer (Bruker, D2 PHASE), a transmission optical microscope (Nikon, Eclipse E600), and a scanning electron microscope (Jeol, JSM-6010PLUS/LA) equipped with EDS.

3. Results and discussion

Figure 2 shows the J–V characteristics of the TiO2/perovskite/spiro-OMeTAD photovoltaic cells under illumination, which indicates the effects of GA and FA addition. The measured photovoltaic parameters of the cells are summarized in Table 1. Standard CH3NH3PbI3(Cl) cells provided a power conversion efficiency (η) of 5.31%, and the averaged efficiency (ηave) of four electrodes on the cells is 4.42%, as listed in Table 1. The short-circuit current density (JSC), open-circuit voltage (VOC), and fill
factor (FF) were increased by GAI addition and the highest efficiency of 12.51% was obtained for the +GAI cell. The highest $J_{SC}$ and $V_{OC}$ were obtained for +GAI +FAI cells, which provided an $\eta$ of 11.66% and a $\eta_{ave}$ of 11.01%. FF values of the +GAI +FAI cells were lower than that of the +GAI cells. Addition of GACl to CH$_3$NH$_3$PbI$_3$(Cl) provided a higher $\eta_{ave}$ of 9.14% than that of the standard cells, but the $\eta$ was lower than that of the +GAI cells.

Table 1 shows that the series resistances ($R_S$) and the shunt resistances ($R_{Sh}$) decreased and increased with GA addition, respectively. These results improved the $J_{SC}$ and $V_{OC}$.

Figure 2 shows the IPCE spectra of these devices. The IPCE of the standard cell was improved in the range of 300–800 nm by GA addition, which resulted in higher current densities than that of the standard cell.

Energy gaps ($E_g$) of the cells that were estimated from the IPCE are listed in Table 1. The $E_g$ values decreased slightly by GA and FA introduction.

Optical microscopy images of the cells are shown in Fig. 4. Microparticles (4–6 μm) were observed for the standard cell, as shown in Fig. 4(a). GAI or GACl addition to the CH$_3$NH$_3$PbI$_3$(Cl) increased the particle size, as shown in Fig. 4 and Table 2 and the surface coverages of the perovskite particles were improved, especially for the +GAI and +GAI +FAI cells, as shown in Figs. 4(b) and 4(d). This effect may be attributed to a promotion of grain growth of the perovskites by long-term heat treatment. For the standard system, the perovskite crystals were decomposed by long-term heat treatment. An improvement in the thermal durability of the perovskite crystals with GA and FA improved the surface morphologies. The photovoltaic properties were improved by the surface morphologies.

An SEM image of the standard cell is shown in Fig. 5(a). Microparticles of 4–6 μm are visible on the mesoporous TiO$_2$ surface, which corresponds to the microparticles in Fig. 4(a). EDS elemental mapping images of the Pb M

![Table 1. Measured photovoltaic parameters of solar cells](image1)

| Device     | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | $\eta_{ave}$ (%) | $R_S$ (Ω cm$^2$) | $R_{Sh}$ (Ω cm$^2$) | $E_g$ (eV) |
|------------|--------------------------|--------------|--------|------------------|-----------------|-------------------|-----------|
| Standard   | 19.0                      | 0.823        | 0.339  | 5.31             | 4.42            | 9.64              | 70        |
| +GAI       | 20.9                      | 0.972        | 0.616  | 12.51            | 11.20           | 7.05              | 1599      |
| +GACl      | 19.1                      | 0.875        | 0.548  | 9.14             | 7.30            | 8.20              | 290       |
| +GAI +FAI  | 21.3                      | 0.999        | 0.547  | 11.66            | 11.01           | 8.92              | 667       |

![Table 2. Measured particle sizes and surface coverages of perovskite layers](image2)

| Device     | Particle size (μm) | Surface coverage (%) |
|------------|--------------------|----------------------|
| Standard   | 5.1 ± 0.67         | 84                   |
| +GAI       | 7.6 ± 0.66         | 94                   |
| +GACl      | 6.7 ± 0.55         | 89                   |
| +GAI +FAI  | 7.4 ± 0.72         | 90                   |
The line, I L line, Cl K line, C K line, and N K line are shown in Figs. 5(b)–5(f), respectively. These elemental mapping images indicate that the particles in Fig. 5(a) correspond to the CH$_3$NH$_3$PbI$_3$(Cl) compound. The Pb, I, and Cl compositions and C:N ratio were calculated from the EDS spectrum by using background correction as listed in Table 3.

Figure 6(a) shows an SEM image of the CH$_3$NH$_3$PbI$_3$(Cl) cell that contains GAI 10 mol%. The surface morphology was changed by GAI addition to the CH$_3$NH$_3$PbI$_3$. The microparticles were larger than those in the standard cell. The growth of the microparticles suppressed pin-holes in the perovskite layers, and the photovoltaic properties were improved. Figures 6(b)–6(f) show EDS elemental mapping images of Pb, I, Cl, C, and N, respectively. The elemental compositions and C:N ratios were calculated from the EDS spectra, and are listed in Table 3. The concentration of Cl compared with Pb is lower than that of the standard cell. Because the GA is substituted at the MA sites in the lattice, excess MA formed CH$_3$NH$_3$Cl with Cl. It is thought that the Cl concentration decreased by CH$_3$NH$_3$Cl volatilization.

Figure 7(a) shows an SEM image of the +GAI+FAI cell. The surface morphology was changed by adding GAI and FAI to the CH$_3$NH$_3$PbI$_3$. Perovskite grains were connected to each other. These networking surface structures suppressed pin-holes in the perovskite layers, and the photovoltaic properties were improved by the surface morphologies. Figures 7(b)–7(f) show EDS elemental mapping images of Pb, I, Cl, C, and N, respectively.
mapping images of Pb, I, Cl, C, and N, respectively. The Cl concentration compared with the Pb is lower than that of the standard cell, which is similar to the +GAI cell.

Figure 8 shows XRD patterns of the perovskite cells. The diffraction peaks can be indexed by a cubic crystal system (Pm\(\bar{3}m\)) for the CH\(_3\)NH\(_3\)PbI\(_3\)Cl) perovskite thin films. The intensities of the 100 and 200 peaks of all perovskite phases are high, because of air-blowing.\(^{50}\) A deformation of the crystal system from the additives was not observed, which indicates that GA and FA addition maintained the cubic crystal structure. Partially substituted GA and FA at the MA site provided a tolerance factor close to 1. This lead to a structural stability of the MA–GA–FA mixed cation-based perovskite crystals.

The measured XRD parameters of the perovskite crystals are listed in Table 4. Lattice constants of +GA or +FA perovskite crystals are larger than that of the standard CH\(_3\)NH\(_3\)PbI\(_3\)(Cl) perovskite crystal. The ionic radii of GA and FA are larger than that of MA,\(^{19}\) and the GA and FA occupied the MA-site partially. Compared with the +GAI system, the +GAI+FAI system showed a larger lattice constant than expected. The crystallite sizes of all perovskites were almost the same for these devices, and GA and FA addition did not affect the crystallite sizes.

Figure 9 shows an increase in the lattice constant of the perovskite crystals by GAI addition. The measured lattice constants for the FAI addition system are also shown for comparison. Because no suitable data exist on a lattice constant of the cubic GAPbI\(_3\) perovskite, the lattice constant of FAPbI\(_3\) was used as a reference value.\(^{52}\) The ionic size of the GA is larger (0.278 nm) than that of the FA (0.253 nm),\(^{53}\) and an increase in lattice constant may be expected for the GAI addition. For the +GAI device, the increase in lattice constant was not linear with the amount of GA added, which indicates that the added GA was not substituted completely at the MA-site. In previous studies, it has been reported that GA was not substituted completely as the cubic perovskite structure when the addition amount was increased to GAPbI\(_3\).\(^{38,54}\) Therefore, it is difficult to substitute MA with GA compared with FA, and these results agreed with the larger lattice constant of the +GAI+FAI system compared with that of the GAI system. No clear relationship was observed between the

| Device       | Lattice constant (nm) | Crystallite size (nm) |
|--------------|-----------------------|-----------------------|
| Standard     | 0.6288                | 64.6                  |
| +GAI         | 0.6293                | 49.2                  |
| +GACl        | 0.6291                | 53.2                  |
| +GAI+FAI     | 0.6303                | 66.3                  |

Fig. 8. (a) XRD patterns of perovskite solar cells. (b) Enlarged XRD peaks at 100 reflection.

Fig. 9. Lattice constant changes for perovskite crystals.
lattice constant and the photovoltaic properties, and the photovoltaic properties would depend on microstructures, such as surface coverages.

From an observation of the carbon distribution in the EDX results in Figs. 5–7, elemental carbon was not detected in some particles. This phenomenon is remarkable for devices with added guanidinium iodide. This indicates that some particles at the surface of the perovskite layer would be PbI₂ precipitates, which were also observed weakly at 2θ of ∼12.6° in the XRD patterns in Fig. 8(a). When more GAi is added, it is necessary to consider the effect of the PbI₂ precipitates. It is also thought that GA is not substituted completely for the MA-site and exists between the PbI₂ precipitates. It is also thought that GA is not substituted completely for the MA-site and exists between particles, as observed in Fig. 9.

4. Conclusions

The photovoltaic performances, such as the $J_{SC}$, $V_{OC}$, $R_S$, and $R_{Sh}$ of MAPbI₃·Cl₂-based perovskite photovoltaic cells were improved by GA addition. An increase in $J_{SC}$ and $V_{OC}$ by GA and FA addition implies that MA–GA–FA mixed-cation-based perovskite solar cells can improve the photovoltaic performances. Microstructural analysis of the perovskite layers indicated that GA addition promoted dense crystalline formation of the perovskite, which suppressed the leakage current and increased the IPCE. The XRD and EDS results indicated that the GA substituted partially at the MA-site.

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