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## Effects of CuBr addition to $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ perovskite photovoltaic devices

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# Effects of CuBr addition to $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ Perovskite Photovoltaic Devices

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**Abstract.** Effects of CuBr addition to perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  precursor solutions on photovoltaic properties were investigated. The  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$ -based photovoltaic devices were fabricated by a spin-coating technique, and the microstructures of the devices were investigated by X-ray diffraction, optical microscopy and scanning electron microscopy. Current density-voltage characteristics were improved by a small amount of CuBr addition, which resulted in improvement of the conversion efficiencies of the devices. The structure analysis showed decrease of unit cell volume and increase of Cu/Br composition by the CuBr addition, which would indicate the Cu/Br substitution at the Pb/I sites in the perovskite crystal, respectively.

## INTRODUCTION

Thin film solar cells with perovskite-type  $\text{CH}_3\text{NH}_3\text{PbI}_3$  compounds have been widely studied recently due to their easy fabrication processes and the high conversion efficiencies [1-4]. After a conversion efficiency of 15% was attained [5], higher efficiencies have been accomplished for various perovskite compounds and device structures, and the conversion efficiencies above 20% were achieved [6-9].

It has been reported that photovoltaic properties of the perovskite solar cells strongly depended on compositions and crystal structures of the perovskite compounds. Metal atom doping, such as tin (Sn) [10,11] antimony (Sb) [12-15], copper (Cu) [16], or arsenic (As) [17], at the lead (Pb) sites have been performed. The optical absorption ranges of the perovskite compounds were expanded by Sn [10,11], and the photoconversion efficiencies of the perovskite solar cells were improved by Sb-, Cu- or As-doping [12-17]. Other elemental doping such as chlorine (Cl) [4,18-21] or bromine (Br) [15,22] at the iodine (I) sites of the perovskite crystals have also been reported. The doped Cl ions could lengthen the diffusion length of excitons, which resulted in the improvement in the conversion efficiency [4]. Further studies on the metal and/or halogen doping at the Pb and/or I sites are fascinating for effects on the photovoltaic properties and microstructures of the perovskite solar cells.

The purpose of the present work was to investigate photovoltaic properties and microstructures of photovoltaic devices with perovskite-type  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  compounds, which were prepared by a simple spin-coating technique in air. Cu is more nontoxic element than Pb. Effects of CuBr 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, X-ray diffraction (XRD), optical microscopy, and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS).

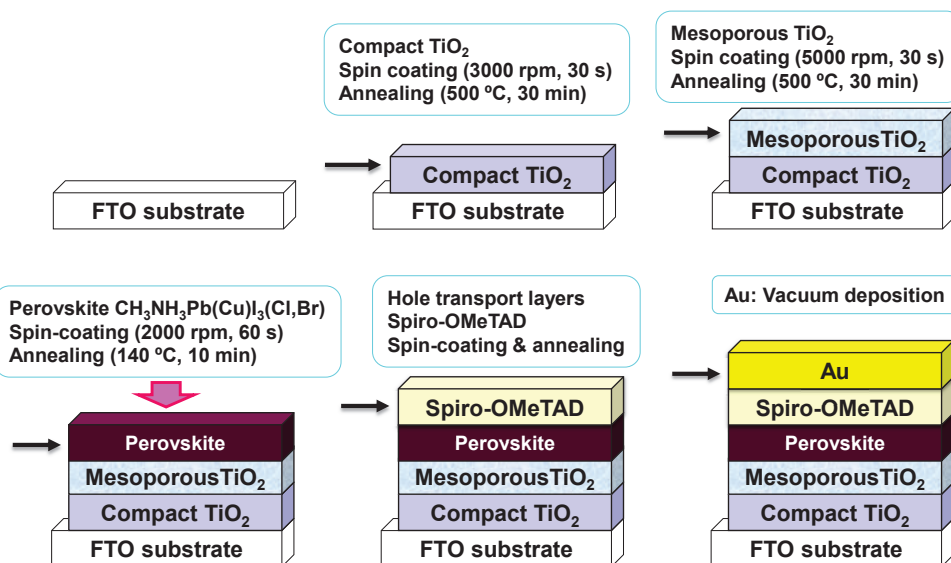
## EXPERIMENTAL

A schematic illustration for the fabrication of the present  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  photovoltaic cells is shown in Fig. 1. Details of the basic fabrication process are described in the reported papers [21,23]. 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  $\text{TiO}_2$  precursor solution was prepared from titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, 0.055 mL and 0.11 mL) with 1-butanol (1 mL), and the 0.15 M  $\text{TiO}_2$  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  $\text{TiO}_x$  layer. Then, the 0.30 M  $\text{TiO}_2$  precursor solution was spin-coated on the  $\text{TiO}_x$  layer at 3000 rpm for 30 s, and heated at 125 °C for 5 min. This process of 0.30 M solution was performed two times, and the FTO substrate was annealed at 500 °C for 30 min to form the compact  $\text{TiO}_2$  layer. For the mesoporous  $\text{TiO}_2$  layer, the  $\text{TiO}_2$  paste was prepared with  $\text{TiO}_2$  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  $\mu\text{L}$ ) and triton X-100 (Sigma-Aldrich, 5  $\mu\text{L}$ ) for 30 min, and was left for 12 h to suppress the bubbles in the solution. After that, the  $\text{TiO}_2$  paste was coated on the substrate by spin-coating at 5000 rpm for 30 s. Then, the cells were annealed at 120 °C for 5 min and at 500 °C for 30 min to form the mesoporous  $\text{TiO}_2$  layer.

For the preparation of the perovskite compounds, a solution of  $\text{CH}_3\text{NH}_3\text{I}$  (Showa Chemical Co., Ltd., 190.7 mg) and  $\text{PbCl}_2$  (Sigma-Aldrich, 111.2 mg) was prepared with a mole ratio of 3:1 in  $\text{N,N}$ -dimethylformamide (DMF, Nacalai Tesque, 500  $\mu\text{L}$ ) at 60 °C for 24 h [18,19].  $\text{CuBr}$  (Sigma-Aldrich) was also added in the solution without decreasing the  $\text{PbCl}_2$  content. The solution of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  was introduced into the  $\text{TiO}_2$  mesopores by a spin-coating method and annealed at 140 °C for 10 min to form the perovskite layer. Then, a hole transport layer (HTL) was prepared by spin-coating on the perovskite layer. For the hole transport layer, a solution of 2,2',7,7'-tetrakis[ $\text{N,N}$ di(p-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, Sigma-Aldrich, 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, 260 mg) in acetonitrile (Nacalai Tesque, 0.5 mL) for 12 h. The former solution with 4-tert-butylpyridine (Aldrich, 14.4  $\mu\text{L}$ ) was mixed with the Li-TFSI solution (8.8  $\mu\text{L}$ ) for 30 min at 70 °C. All procedures for preparation of the thin films were performed in ordinary air. Finally, gold (Au) contacts were evaporated as top metal electrodes. Layered structures of the present solar cells were denoted as  $\text{FTO}/\text{TiO}_2/\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})/\text{spiro-OMeTAD}/\text{Au}$ , as shown in Fig. 1.

$J$ - $V$  characteristics of the photovoltaic cells were measured under illumination at 100  $\text{mW cm}^{-2}$  by using an AM 1.5 solar simulator (San-ei Electric, XES-301S). The  $J$ - $V$  measurements were performed by source measure unit (Keysight, B2901A Precision SMU). The scan rate and sampling time were  $\sim 0.08 \text{ V s}^{-1}$  and 1 ms, respectively, and averaged values of forward and reverse scans were used for the photovoltaic parameters. Four cells were tested for each condition. The solar cells were illuminated through the side of the FTO substrates, and the illuminated area was 0.090  $\text{cm}^2$ . The microstructures of the present cells were investigated by using an X-ray diffractometer (Bruker, D2 PHASER), a transmission optical microscope (Nikon, Eclipse E600) and a scanning electron microscope (Jeol, JSM-6010PLUS/LA) equipped with EDS.



**FIGURE 1.** Schematic illustration for the fabrication process of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  photovoltaic devices using  $\text{TiO}_2$  nanoparticles.

## RESULTS AND DISCUSSION

The  $J$ - $V$  characteristics of the  $\text{TiO}_2$ /perovskite/spiro-OMeTAD photovoltaic devices under illumination are shown in Fig. 2, which indicates effects of CuBr addition to the  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  device. Measured photovoltaic parameters of the devices are summarized as Table 1. The  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  device provided a power conversion efficiency ( $\eta$ ) of 7.31%, a fill factor ( $FF$ ) of 0.609, a short-circuit current density ( $J_{SC}$ ) of  $14.4 \text{ mA cm}^{-2}$ , and an open-circuit voltage ( $V_{OC}$ ) of 0.832 V. Power conversion efficiencies of the devices depended on the amount of CuBr addition. The highest efficiency was obtained for the 1% CuBr-added  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ , which provided an  $\eta$  of 9.40%, a  $FF$  of 0.647, a  $J_{SC}$  of  $17.3 \text{ mA cm}^{-2}$ , and a  $V_{OC}$  of 0.841 V. A decrease in the series resistance ( $R_s$ ) and an increase in the shunt resistance ( $R_{sh}$ ) of the present CuBr-added cells were also observed, as indicated in Table 1. Cu addition would lead to a reduction in  $R_s$  and an improvement in the  $J_{SC}$ . A decrease in the leakage current and an increase in  $R_{sh}$  resulted in improved  $FF$  values.

Optical microscope images of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  cells are shown in Fig. 3. Microparticles are observed for the cells with CuBr, as shown in Fig. 3(b)-3(d), compared with the standard  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  cells. Perovskite crystals with sizes of  $\sim 5 \mu\text{m}$  are observed at the surface of the mesoporous  $\text{TiO}_2$ . This microstructures would improve the photovoltaic properties, as well as the doping effect of Cu and Br at the Pb and I/Cl sites, respectively. When 5% CuBr was added, larger crystals with a size of  $\sim 10 \mu\text{m}$  are also observed, as shown in Fig. 3(d).

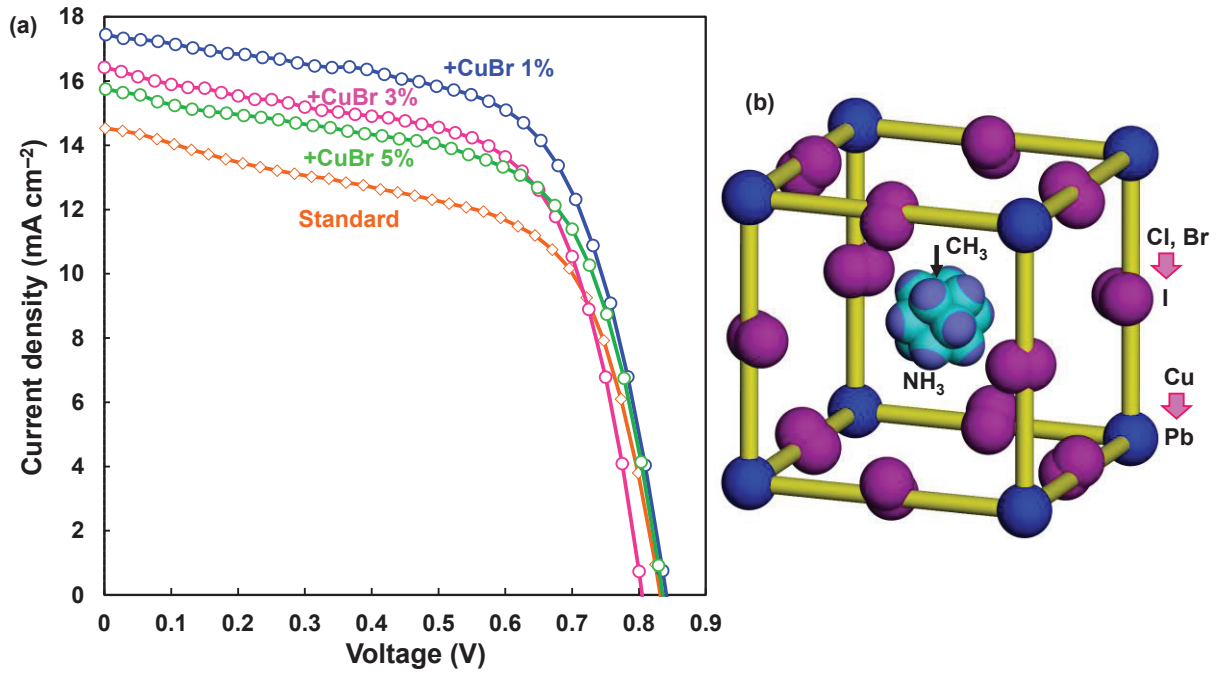
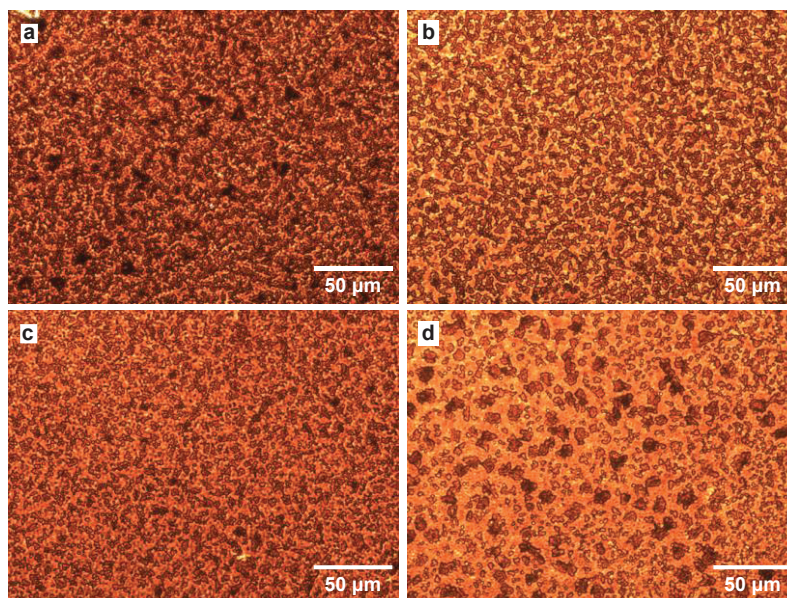


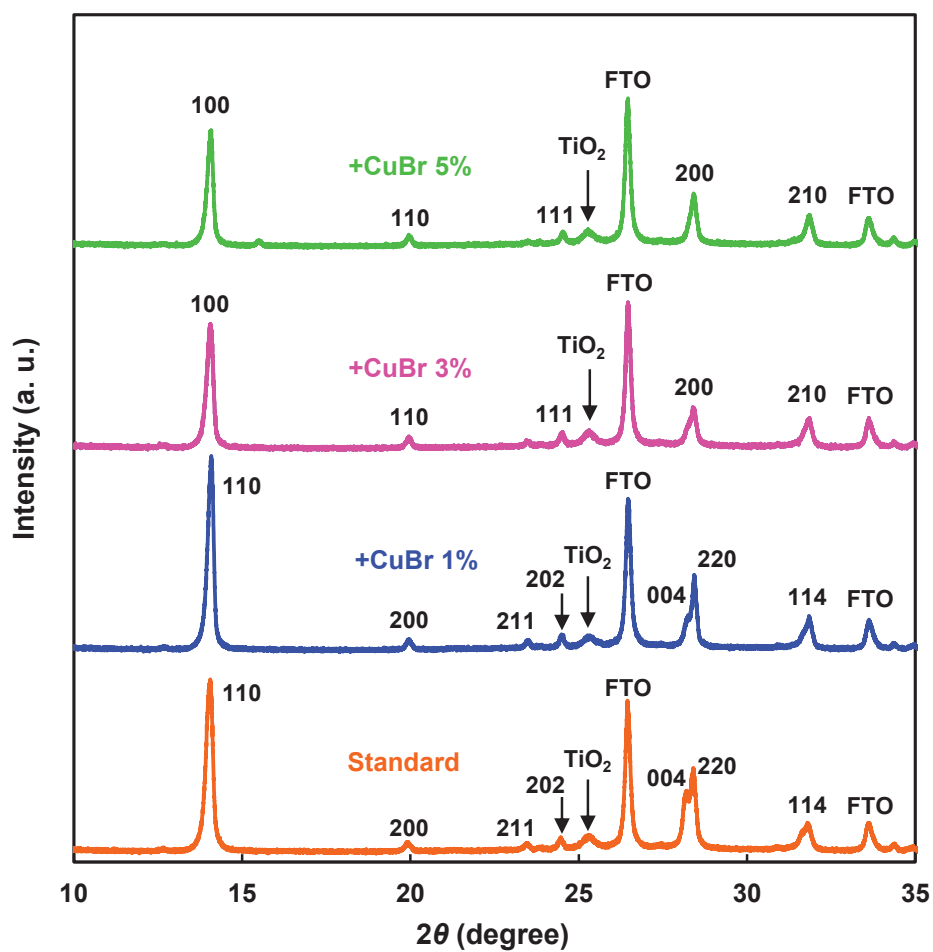
FIGURE 2. (a)  $J$ - $V$  characteristics of the present  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  photovoltaic devices. (b) Structure model of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$ .

TABLE 1. Measured photovoltaic parameters of the present photovoltaic devices.

| Devices  | $J_{SC}$<br>( $\text{mA cm}^{-2}$ ) | $V_{OC}$<br>(V) | $FF$  | $\eta$<br>(%) | $R_s$<br>( $\Omega \text{ cm}^2$ ) | $R_{sh}$<br>( $\Omega \text{ cm}^2$ ) |
|----------|-------------------------------------|-----------------|-------|---------------|------------------------------------|---------------------------------------|
| Standard | 14.4                                | 0.832           | 0.609 | 7.31          | 7.26                               | 281                                   |
| +CuBr 1% | 17.3                                | 0.841           | 0.647 | 9.40          | 6.89                               | 498                                   |
| +CuBr 3% | 16.3                                | 0.805           | 0.636 | 8.33          | 5.77                               | 360                                   |
| +CuBr 5% | 15.7                                | 0.835           | 0.630 | 8.25          | 6.33                               | 370                                   |



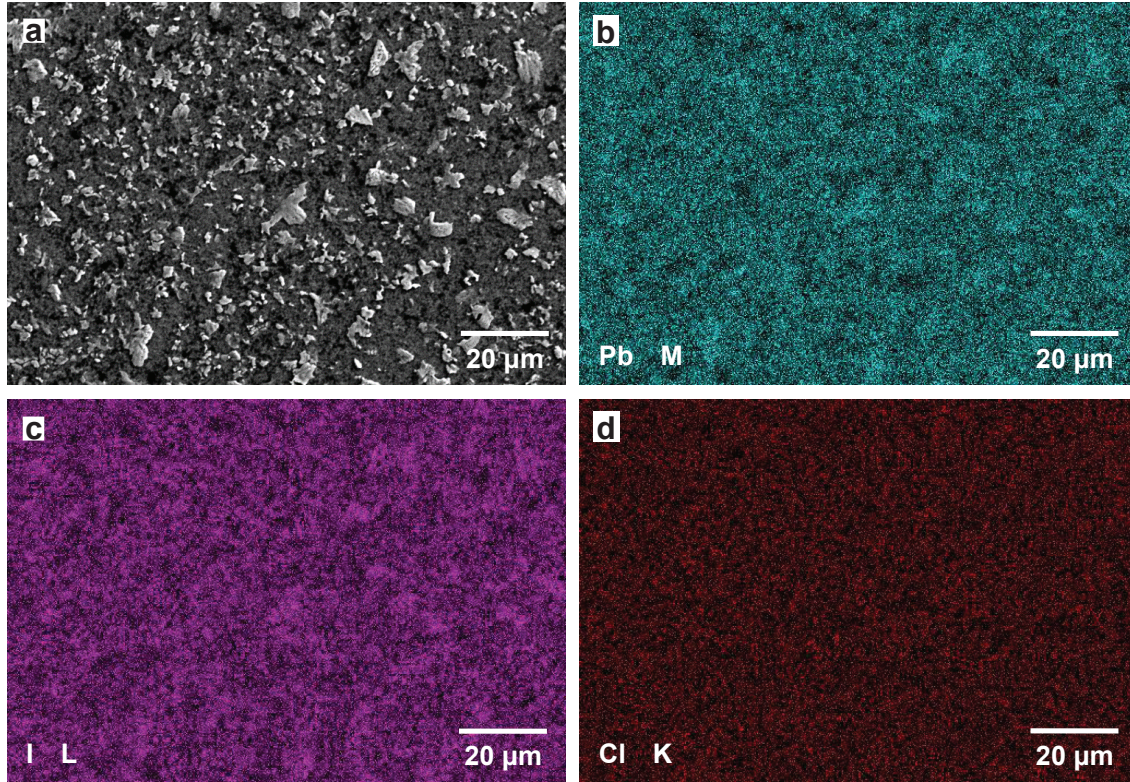
**FIGURE 3.** Optical microscope images of (a) standard  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ , (b) +CuBr 1%, (c) +CuBr 3%, and (d) +CuBr 5% cells.



**FIGURE 4.** XRD patterns of  $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$  photovoltaic devices.

**TABLE 2.** Measured structural parameters of the present photovoltaic devices.  $V$ : unit cell volume.  $Z$ : number of chemical units in the unit cell.

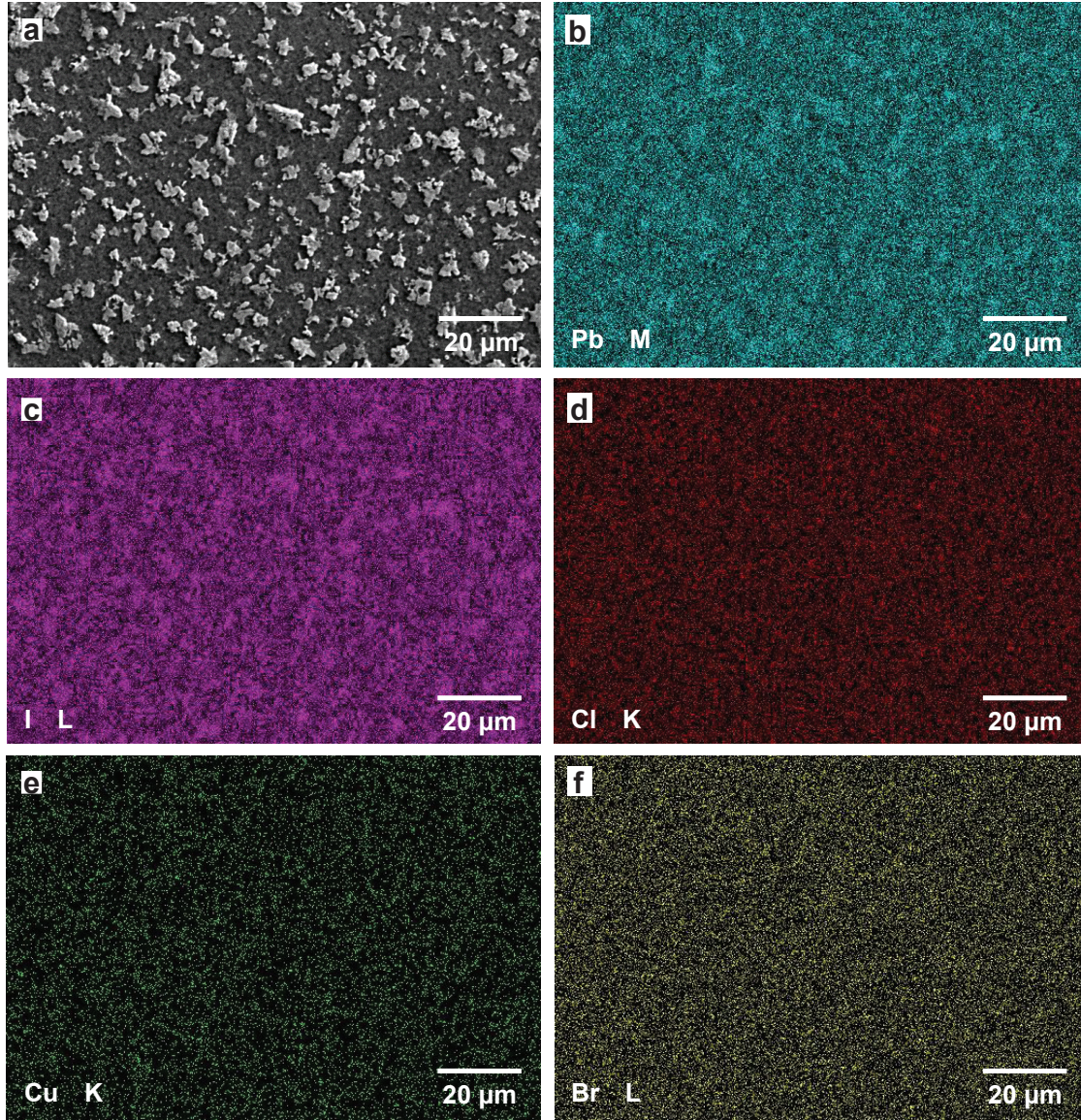
| Devices  | Crystal system | Lattice constants<br>(Å)   | $V$ (Å <sup>3</sup> ) | $Z$ | $V/Z$ (Å <sup>3</sup> ) |
|----------|----------------|----------------------------|-----------------------|-----|-------------------------|
| Standard | Tetragonal     | $a = 8.874$<br>$c = 12.65$ | 996.2                 | 4   | 249.0                   |
| +CuBr 1% | Tetragonal     | $a = 8.875$<br>$c = 12.63$ | 994.8                 | 4   | 248.7                   |
| +CuBr 3% | Cubic          | $a = 6.281$                | 248.1                 | 1   | 248.1                   |
| +CuBr 5% | Cubic          | $a = 6.274$                | 247.0                 | 1   | 247.0                   |



**FIGURE 5.** (a) SEM image of  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  cell. Elemental mapping images of (b) Pb M line, (c) I L line, and (d) Cl L line.

Figure 4 is XRD patterns of the present  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  cells. The diffraction reflections can be indexed by a tetragonal crystal system ( $I4/mcm$ ) for the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  cells. Split diffraction peaks of 004–220 at  $2\theta$  of  $\sim 28^\circ$  for the standard cell changed into diffraction peaks of 200 by increasing the amount of CuBr addition, which indicates the structural transformation from the tetragonal to cubic crystal system ( $Pm-3m$ ) [23,24]. Measured structural parameters of the present photovoltaic devices are summarized as Table 2. With increasing the amount of CuBr addition, the unit cell volume was decreased, which would be due to the small ionic sizes of Cu and Br compared with Pb and I.

Figure 5(a) shows a SEM image of  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  cell, and microcrystals with various sizes in the range of 2–20  $\mu\text{m}$  are observed. Elemental mapping images of Pb, I, and Cl by SEM-EDS are shown in Figs. 5(b)–5(d), respectively. The elemental mapping images indicate that the particles observed in Fig. 5(a) correspond to the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  compound. The composition ratios of the elements Pb, I, and Cl were calculated from the EDS spectrum using background correction by normalizing the spectrum peaks, as listed in Table 3. This result indicates that I might be deficient from the starting composition of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .



**FIGURE 6.** (a) SEM image of  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  cell. Elemental mapping images of (b) Pb M line, (c) I L line, (d) Cl K line, (e) Cu K line, and (f) Br L line.

**TABLE 3.** Measured compositions of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$  cells.

| Devices  | Pb<br>(at.%) | Cu<br>(at.%) | I<br>(at.%) | Cl<br>(at.%) | Br<br>(at.%) |
|----------|--------------|--------------|-------------|--------------|--------------|
| Standard | 32.9         | 0            | 59.6        | 6.9          | 0            |
| +CuBr 3% | 33.0         | 0.23         | 58.4        | 7.0          | 1.3          |

A SEM image of  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  cell added with 3% CuBr is shown in Fig. 5(a). By adding CuBr to the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ , the surface morphology was changed, and crystals with the sizes of  $\sim 5 \mu\text{m}$  are observed, which would be due to an effect of CuBr addition. Elemental mapping images of Pb M line, I L line, Cl K line, Cu K line, and Br L line are shown in Figs. 5(b)-5(f), respectively, and the images indicate the perovskite phase is dispersed homogeneously on the photovoltaic device. These homogeneous surface structures would improve the photovoltaic

properties. From the SEM-EDS results, Cu and Br elements were detected, and the compositions of I decreased, and the deficient I might increase the hole concentration.

Two assumed mechanisms could be considered for the increase of the photoconversion efficiencies. The first mechanism is as follows: when a small amount of Cu was doped in the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  phase, carrier concentration in the perovskite phase would be increased by the CuBr addition, which would result in the increase of the  $J_{\text{SC}}$  values. The second is as follows: the homogeneous surface and interfacial structures formed by adding CuBr to the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ , which improved the photovoltaic properties, especially the  $FF$  values. Further studies are necessary for precise structure determination of the devices.

## CONCLUSION

$\text{CH}_3\text{NH}_3\text{Pb}(\text{Cu})\text{I}_3(\text{Cl},\text{Br})$ -based photovoltaic devices were fabricated by a spin-coating technique, and effects of CuBr addition to the perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  precursor solutions on the photovoltaic properties were investigated. The microstructures of the devices were investigated by XRD and SEM-EDS. The unit cell volume of the perovskite phase was slightly decreased by adding a small amount of CuBr, and the Cu/Br composition increased. This would indicate Cu/Br substitution at the Pb/I sites in the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  perovskite crystal. Carrier concentration in the perovskite phase would be increased by the CuBr addition, which would result in the increase of the  $J_{\text{SC}}$  values and the conversion efficiencies to 9.4%.

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