

Effects of co-addition of NaCl and CuBr₂ to CH₃NH₃PbI_{3-x}Cl_x perovskite photovoltaic devices

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Abstract

The lattice constant of CH₃NH₃Pb(Cu)I_{3-x}Cl_x(Br) is slightly increased by the addition of NaCl, and the X-ray diffraction peaks corresponding to the tetragonal symmetry disappears after several weeks, which indicates a structural transition from the tetragonal to cubic system by the co-addition of NaCl and CuBr₂. A microstructural model, where Na occupies the CH₃NH₃ vacancy site, is proposed. The conversion efficiency is maintained for 10 weeks for the device with a co-addition of CuBr₂ and NaCl.

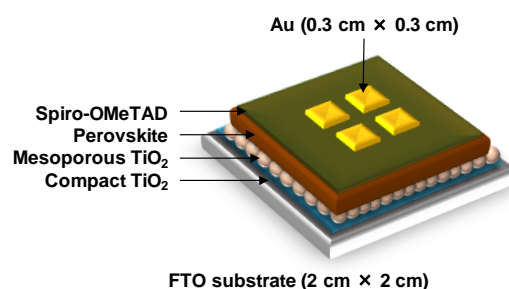


Fig. 1. Structure of the perovskite photovoltaic cell.

1. Introduction

CH₃NH₃PbI_{3-x}Cl_x-type compounds have been widely studied [1-2]. These perovskite compounds can be formed by reacting a mixture of the precursors CH₃NH₃I and PbCl₂ in a 3:1 molar ratio. In our previous work, photovoltaic properties of perovskite solar cells were improved by the simultaneous addition of alkali metal iodides and CuBr₂ to the perovskite precursors [3].

The purpose of the present study is to fabricate NaCl/CuBr₂ co-added MAPbI_{3-x}Cl_x photovoltaic devices in air and to characterize the photovoltaic properties and crystal structures. The additive quantities of NaCl and CuBr₂ to the perovskite precursor solutions are optimized to improve the photovoltaic performance and stability of the perovskite solar cells.

2. Experimental

The 0.15 M TiO₂ precursor solution was spin-coated on the FTO substrate and the coated substrate was then annealed at 125 °C for 5 min. Then, the 0.30 M TiO_x precursor solution was spin-coated on the TiO₂ layer and the resulting substrate was annealed at 125 °C for 5 min. The process for forming the 0.30 M precursor layer was performed twice. Then, the FTO substrate was sintered at 550 °C for 30 min to form a compact TiO₂ layer. The mesoporous TiO₂ layer was spin-coated on the compact TiO₂ layer. The resulting cell was heated at 125 °C for 5 min and then annealed at 550 °C for 30 min. The Perovskite solutions with 1–10% NaCl and 1–10% CuBr₂ of PbCl₂ molar were then introduced into the TiO₂ mesopores by spin coating, followed by annealing at 140 °C for 10 min in air. Then, spiro-OMeTAD was spin-coated on the perovskite layer. Finally, gold (Au) electrodes were evaporated as top electrodes using a metal mask for the patterning. Fig. 1 shows the structure of the perovskite photovoltaic cell.

3. Results and discussion

The device added with 2% NaCl and 2% CuBr₂ provided a J_{SC} of 22.7 mA cm⁻², V_{OC} of 0.944 V, FF of 0.676, and η of 14.5%. The V_{OC} of the device added with NaCl was higher than that of the device added with NaI, owing to the effect of Cl addition. The hysteresis index value was decreased by the co-addition of 2% CuBr₂ and 2% NaCl, which contributed to suppress the recombination between a hole and an electron. The remained Cl in the perovskite layer would play a critical role in the perovskite grain growth, which resulted in the few defects in perovskite thin films, and also lead to the stability.

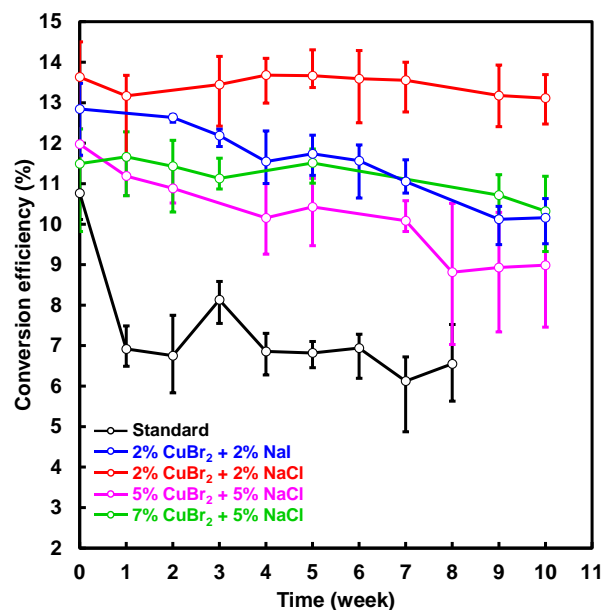


Fig. 2. Changes in conversion efficiency for the present perovskite photovoltaic devices.

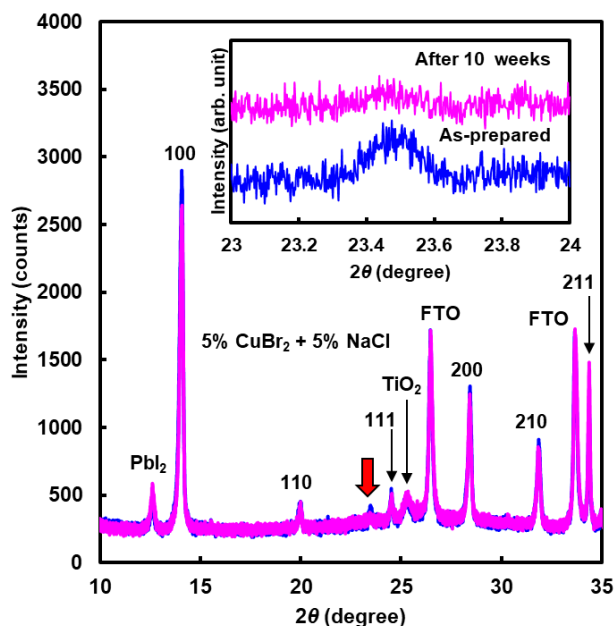


Fig. 3. XRD patterns of (a) (5% CuBr₂ + 5% NaCl)-added devices.

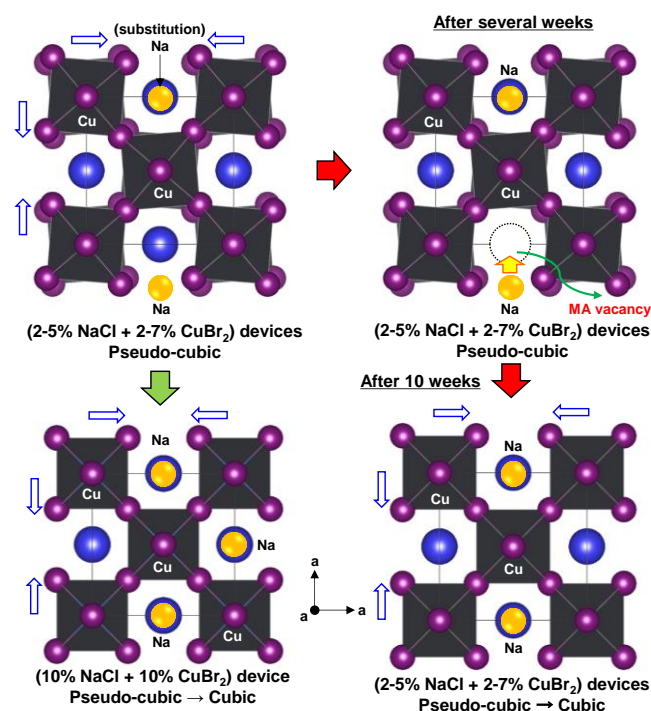


Fig. 4. Schematic illustration of the stability mechanism for the Na-added perovskite crystals.

Fig. 3 shows the XRD patterns of the present devices after 10 weeks. As indicated by the red arrows, diffraction peaks corresponding to a tetragonal symmetry disappeared by the addition of NaCl, which indicated a structural transition from a tetragonal to cubic system after 10 weeks to contribute to the stability of the devices. The lattice constant decreased slightly after 10 weeks. Although the lattice constants were expected to decrease owing to the smaller ionic radii of Na and Cl, increases of lattice constants were observed for the 2% NaCl-added devices, which suggested that the added Na occupied the interstitial sites in the perovskite crystal lattice, as shown in Fig. 4. The partial Na would transfer into the MA vacancy site after 10 weeks, which caused the structural transformation from pseudo-cubic system to cubic system. This structural change indicated that a small amount of Na improved the stability of the photovoltaic properties. Although the present perovskite structures exhibited an almost cubic structure from the lattice constant, weak diffraction peaks corresponding to tetragonal symmetry were observed at $\sim 23^\circ$, as shown in Fig. 3, and this structure was classified as pseudo-cubic almost of a/c axis was 1 in the present work.

The basic reaction for the perovskite formation is expressed as $3\text{MAI} + \text{PbCl}_2 \rightarrow \text{MAPbI}_3 + 2\text{MACl}$ (†), and the MACl compound vaporized during annealing. Excess addition of Cl⁻ induced MACl evaporation upon annealing the perovskite layer, and many pinholes were formed by desorption of the MACl. Further addition of Na and Cl provided local distributions of the Na and Cl, and MA(Na)PbCl₃(I,Br) crystals were finally formed on the surface of the perovskite layer by the excess addition of NaCl, as shown in Fig. 5. The highest trap density of $1.94 \times 10^{16} \text{ cm}^{-3}$ was observed for 2% CuBr₂-added device, which indicates the trap-assisted recombination occurred by the CuBr₂ addition. On the other hand, the trap density were decreased and the trap-assisted recombination was suppressed by the 2% NaCl addition. Furthermore, the lowest trap density was obtained by the simultaneous addition of 2% CuBr₂ and 2% NaCl, which agreed with the result that the most stable photovoltaic performance was obtained for the (2% CuBr₂ + 2% NaCl)-added device.

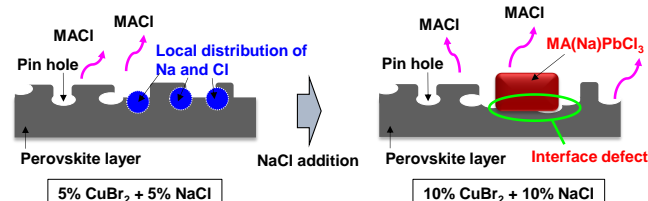


Fig. 5. Schematic illustration of the perovskite layer formation mechanisms.

References

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