CRYSTAL STRUCTURE ANALYSIS OF PEROVSKITE CH$_3$NH$_3$PbI$_3$ SOLAR CELLS BASED ON RIETVELD REFINEMENT

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Last several decades, the requirement for an environmentally sustainable energy source has driven extensive research aimed at achieving high efficiency and low cost photovoltaic generation devices. Particularly, perovskite solar cells (PSCs) have attracted keen interest as a prime candidate that meets these requirements. Meanwhile, Rietveld refinement was widely used to study microstructures of crystalline materials. However, this technique has seldom been applied for PSCs. Fu et al. [1] applied this technique to determine the lattice parameters of CH$_3$NH$_3$PbI$_3$ in the PSC configuration. However, they determined just lattice constants, and there was no description on the precise crystal structure including positions or site occupancies of each atom composing CH$_3$NH$_3$PbI$_3$.

The aim of this work is to study precise crystal structures including atomic positions and site occupancies of perovskite CH$_3$NH$_3$PbI$_3$ films in the PSC configuration. The analyzed solar cells were fabricated using the standard PSC processing techniques in our laboratory. In these devices, the electron transport layer consisting of compact TiO$_2$ and mesoporous TiO$_2$, the CH$_3$NH$_3$PbI$_3$ light absorber, and the hole transport layer consisting of 2,2',7,7' - tetrakis[N,N-di(p-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-OMeTAD) were coated in sequence on the fluorine-doped thin oxide (FTO) substrate. The X-ray diffraction (XRD) measurement was carried out for the solar cell by using D2 PHASER (Bruker). The theoretical XRD profile was then refined by using RIETAN-2000 [2], until it matches the measured profile. As the crystal structure, we assumed the realistic model including the disordered effects [3] as shown in Figure 1 (a). Introducing this model into the Rietveld program, we have optimized atomic positions and site occupancies of CH$_3$NH$_3$PbI$_3$. As a result, satisfactory agreement with the measurement was obtained with an R-factor of as low as 3%. A refined composition ratio of Pb, methylammonium (MA), and I (Pb:MA:I) coincided with the ideal value of 1:1:3. For comparison, a similar optimization was carried out based on the simplified crystal structure model. In this model, Pb cation sits at cube corner positions (0, 0, 0), MA cation sits at a body center position (1/2, 1/2, 1/2), and I anion sits at edge centred positions (0, 0, 1/2), as shown in Figure 1 (b). In this case, the R-factor was similar to that of the realistic model. However, the composition ratio was largely deviated from the identical value. This result suggests the oversimplified crystal structure would introduce serious errors in the estimation of the occupancies.

Figure 1: (a) Realistic and (b) simplified crystal structures of CH$_3$NH$_3$PbI$_3$

References