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Investigation of A-site substitution of Sn-Perovskite on the solar cells performance

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Abstract

In this study, the performance of tin-based perovskite solar cells are compared by substituting A site cations with various ionic radii. In the composition of $Q_{0.1}(FA_{0.75}MA_{0.25})_{0.9}SnI_3$, Q is replaced with Na^+, K^+, Cs^+, EA^+ and BA^+, respectively, and the relationship between the lattice strain and photovoltaic performances are discussed. The lattice strain is smallest when 10 mol% EA^+ is substituted showing an efficiency of 5.41%.

1. Introduction

Sn perovskite solar cell is one of the most anticipated candidates to replace the more toxic Pb-based perovskite solar cells (PSCs) which could rival the efficiency of Pb PSCs. It is well known that the stability of perovskite structure is dependent on the tolerance factor.[1] In Pb PSCs, it has been reported that the tolerance factor is adjusted by the substitution of A site cations with different ionic radii to increase the efficiency solar cell.[2-4] Similar to Pb PSCs, there are reports on improving the device performance of Sn PSCs by introduction of Cs cation and Guanidinium cation.[5, 6] However, in the case of Sn-based perovskites, the relation between the perovskite crystal and tolerance factor has never been reported. This prompted us to introduce multi-cation in the A site of $ASnX_3$ structure, and to clarify the relationship between the lattice strain from XRD data and the solar cells efficiency.

2. General Instructions

Device fabrication

The solar cell has an inverted structure consisting of glass/ ITO/ PEDOT:PSS (40nm)/ Sn perovskite (160-180nm)/ PCBM (20nm)/ C60 (20nm)/ BCP (6nm)/ Ag (60nm)/ Au (30nm) layer. PEDOT:PSS is spin-coated at 5000 r.p.m. for 50 s and heated at 140 ºC for 20 mins. Followed by perovskite layer which is spin-coated at 5000 r.p.m. for 50 s. The film is annealed at 70 ºC for 10 mins. Chlorobenzene is used as the anti-solvent for the perovskite. PCBM is then spin-coated on the perovskite layer at 2000 r.p.m. for 60 s. C60, BCP, Ag and Au are deposited by vapor deposition under high vacuum.

Result and Discussion

In this paper, we prepared Sn-based perovskites with the following structure $Q_x(FA_{0.75}MA_{0.25})_{1-x}SnI_3$, where, Q was replaced with Na+, K+, Cs, EA+ and BA+, respectively. For all cations, the substitution concentration was fixed at 10 mol%, except for BA^+ where 2 concentrations (5 mol% and 10 mol%) were studied. Q-substituted Sn perovskites were denoted as Na-10%, K-10%, Cs-10%, FAMA, EA-10%, BA-5% and BA-10% for simplification. Tolerance factor (t) was calculated by the following equation.[7]

$$t = \frac{r_A + r_X}{\sqrt{2}\ (\ r_B + r_X)} \qquad (1)$$

where r_B and r_X are effective ionic radii of B divalent metals and X halide ions, respectively. When t value lies in the range of 0.8 – 1.06, cubic perovskite structures with high stability are formed.[7] r_A are calculated by the following equation.

$$r_A = xr_Q + (1-x)(0.75r_{FA} + 0.25r_{MA}) \quad (2)$$

where r_{FA}, r_{MA} and r_Q represents effective ionic radii of FA^+, MA^+ and Q cation, respectively, and x is the concentration of

Q cation substituted for Sn perovskite.

Lattice strain (ε) was calculated by Williamson-Hall plot using the following equation.[8-11]

$$\beta cos\theta = \frac{K\lambda}{Dcos\theta} + 4\varepsilon sin\theta \qquad (3)$$

where β is the full width half maximum of Bragg's peak assigned to the perovskite crystal, θ is the Bragg's peak position, D is the average crystallite size, K is the sharp factor

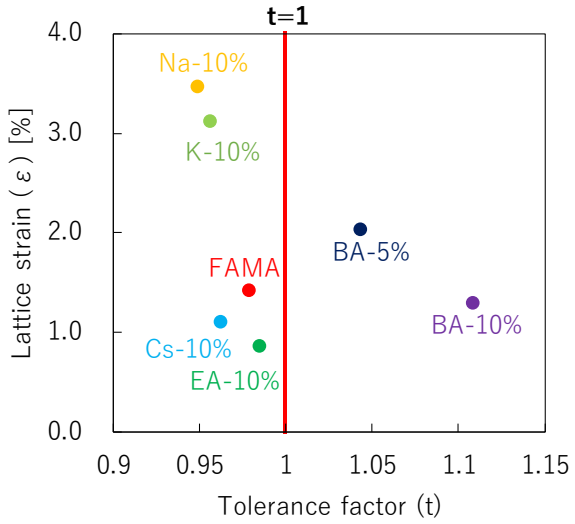

Figure 1. Relationship between the lattice strain and tolerance factor for Sn perovskite substituted with various Q cations.

(K=0.94), and λ is the x-ray wavelength of CuK_α in nanometers

(λ=0.154nm).[10] Figure 1 shows the relationship between the lattice strain and tolerance factor for Sn perovskite substituted with various Q cations. Na-10% showed the lowest tolerance factor of 0.949 and the corresponding lattice strain was 3.46%.

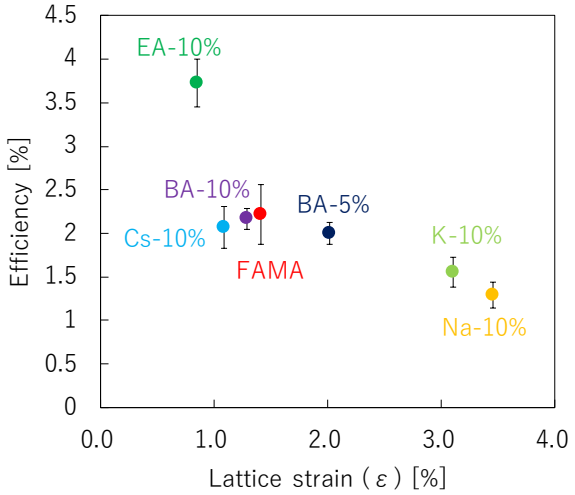

Figure 2. Relationship between solar cell efficiency and the lattice strain for Sn perovskite substituted with various Q cations.

Subsequently, as the radius of Q cations increased to K^+, Cs^+, and EA^+, the tolerance factor approached 1.0 and the lattice strain decreased. The smallest lattice strain was observed with EA-10%. When 5 mol% of BA^+ was substituted, the tolerance factor exceeded 1.0 and the lattice strain also increased. However, when 10 mol% of BA^+ was substituted, the lattice strain was reduced due to the change of the perovskite from 3D to 2D/3D perovskite. Figure 2 shows the relationship between the solar cell efficiency and the lattice strain for Sn perovskite substituted with various Q cations. The efficiency of the EA-10% with the smallest lattice strain was the highest 4.26%. For K-10% and Na-10% with bigger lattice strain with efficiencies lower than those of other devices. Next, we evaluated the electronic properties including the carrier concentration, carrier mobility, PL life time and diffusion length for these perovskite layers. A clear correlation between the lattice strain, carrier concentration and carrier life time were not observed. However, the smaller the lattice strain, the better the as carrier mobility and diffusion length. Cs-10% and EA-10% have the highest mobility which decreased with an increase in the relative lattice strain in the following order: Cs-10% =EA-10% >BA-10% >FAMA >BA-5% >K-10% >Na-10%. EA-10% with the lowest lattice strain showed an efficiency of 5.41% after storing 4 days in globe box.

3. Conclusions

As a conclusion, the substitution of A site in tin-based perovskites, we have established a direct relationship between the lattice strain and the tolerance factor. Among all the electronic properties, the relative lattice strain showed good relationship with carrier mobility and carrier diffusion length. It was proved that the solar cell efficiency for Sn-perovskite showed a direct relationship with the relative lattice strain. The results will provide design directions to Sn-based PSCs with high efficiency.

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