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ペロブスカイト太陽電池向け非鉛材料の探索

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Exploration of Pb-Free Halide Perovskite Materials for Solar Cell Applications

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鉛フリーペロブスカイトの候補として FASnI3 と BiI3 を検討した。スズ系ペロブスカイト（Sn-PSC）については Rb 元素を添加する手法を開発し、光電変換特性が 3.12%から 5.89%へ向上した。本手法により Sn-PSC の結晶性をある程度制御する事が可能となった。

Bi ベースの太陽電池については、さまざまな条件下で結晶化させる手法を開発して BiI3 膜の特性を検討し、倒立型デバイスにて約 1.02%の光電変換特性が得られた。本手法により様々なオプトエレクトロニクスアプリケーション向けに BiI3 材料をさらに最適化する事が可能となり得る。

Leading to our proposal for Pb-free perovskite, we have explored FASnI3 and BiI3 as an alternative Pb-PSCs. For Sn-PSCs, the Rb incorporated $FASnI_3$ leads the improvement in device with the PCE of control device (3.12%) to 5.89% for $(Rb,FA)SnI_3$. This work paves the way for optimizations of Sn-HaP film quality by modulating the crystal lattice for boosting the performance and stability device.

For Bi-based solar cells, I have investigated the crystallized BiI3 films under various ambient conditions. The inverted device demonstrated the best PCE~1.02%. This work opens up multiple aspects for further optimization of BiI3 material for other optoelectronic applications.

1. 研究内容

A. Sn-halide perovskite solar cells:

Among these alternatives, Sn-based halide perovskites (Sn-HaP), a close cousin to Pb-HaP, are promising alternatives. In this report, we have studied the role of Rb incorporation (i.e. smaller cation in A-site) into the lattice structure of $FASnI_3$ for device efficiency and insight into device analysis.

I. Device fabrication method: For the fabrication of Sn-HaP films, the precursors were prepared by dissolving FAI, SnI_2, and SnF_2 adding different concentrations of RbX in DMSO solvent. As depicted in the schematic of device fabrication (Fig. 1), we prepared inverted Sn-PSCs with PEDOT: PSS (HTL), $PC_{61}BM$ (ETL) by spin coating, AZO (ESL) and Ag deposited by thermal evaporation. Khadka et al. J. Mater. Chem. C, 8, 2307-2313, (2020).

II. Results and Summary:

The films with RbCl additive exhibit a significant improvement in film coverage by suppressing the pinhole's densities (Fig. 2a-d). We observed highly oriented crystallographic planes of (100) and (200) for Sn-HaP films with RbCl additive whereas the pristine film grows with multiple crystal orientations (Fig. 3e,f). The absorption spectra of the films (x=0-0.12) (Fig. 3g) demonstrate some effects with a higher content of RbCl additive. Photoluminescence (PL) spectra of the corresponding films (Fig. 3h) display a slight redshift with the higher RbCl content. It is observed that the RbCl additive facilitates uniform morphology with better crystal quality and suppression of oxidation of Sn^{2+}. This results in an enhancement in the device efficiency of 3.12% for pure Sn-HaP to 5.89% for Rb-incorporated ($Rb_{0.08}FA_{0.92}SnI_3$) absorber layer (Fig. 3c) with higher reproducibility and superior stability (Fig.3a). The device analysis corroborates that the incorporation of Rb in the $FASnI_3$ structure plays a crucial role in ameliorating film growth, surface chemistry, and mitigation of trap centers (Fig. 3b).

B. Bi-halide based solar cells:

Several Pb free photovoltaic absorbers; Sn, Ge, Bi, and Sb-based halide semiconductor materials have centred the research focus for alternative materials. Both Pb^{2+} and BiI^{+3} are highly polarizable cations with large spin-orbit coupling effects. As another Pb-free candidate, the BiI_3 (Eg~1.75 eV) based devices films were investigated and prepared device adopting inverted device structure. We found the BiI_3 device is more stable than the Pb and Sn-based HaP devices.

I. Device fabrication method:

The bismuth triiodide (BiI_3) film was prepared by spin BiI_3 precursor solution (100 mg/mL) in DMF. The schematics of film fabrication and crystallization by annealing under controlled solvent vapour conditions are shown in Fig.4.

II. Results and Summary:

We report on the solution-processed BiI3 solar cells and their optoelectronic properties under different fabrication approaches. The BiI_3 films crystallized by annealing under controlled solvent vapour conditions were found to have dominant effects on film morphology as well as the crystal growth as depicted in Fig. 5.

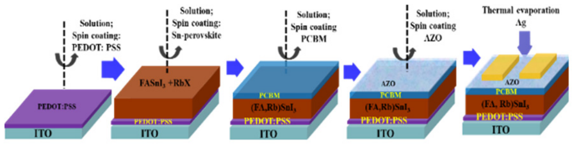

Fig.1 Schematics of fabrication of Sn-perovskite devices.

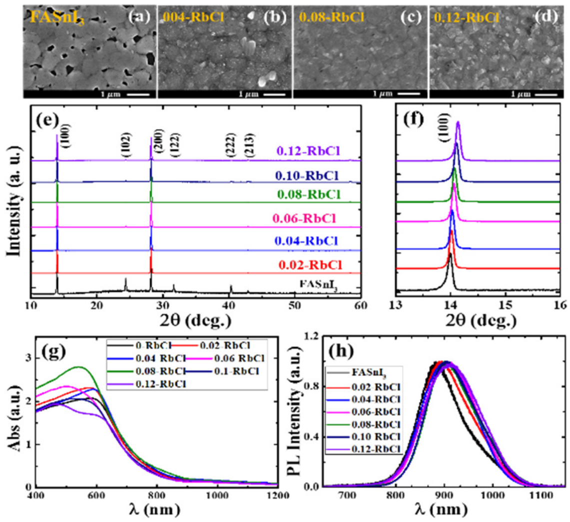

Fig. 2. *SEM images of Sn-HaP film with RbCl additive (a-d). XRD patterns (e,f), absorption spectra (g), and PL spectra (h).*

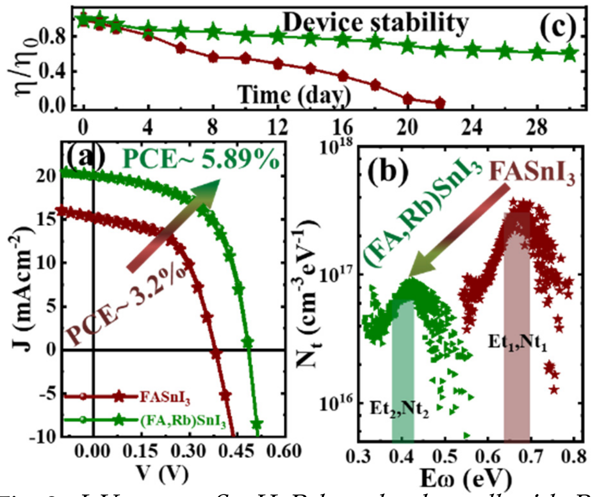

Fig. 3. *J-V curves Sn-HaP based solar cell with Rb additive(a). Defect density profile (b), device stability under ambient condition (c).*

We have fabricated an inverted device structure; ITO/PTAA/BiI_3/PCBM/BCP/Ag with BiI_3 film processed by annealing under solvent vapour conditions as depicted in Fig. 6a, b. The J-V characteristics of corresponding conditions are shown in Fig. 6c. The photovoltaic device with BiI3 film followed by annealing under chlorobenzene vapour atmosphere demonstrated the best power

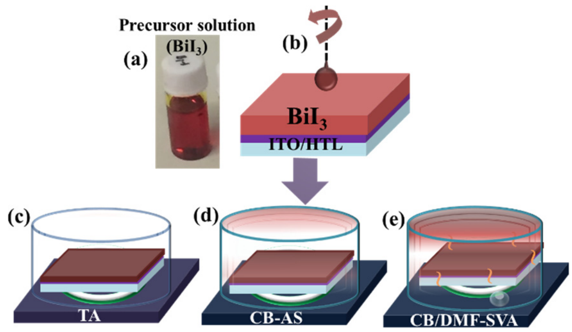

Fig. 4. *Schematic of the fabrication approach of the BiI_3 thin film. (a) Precursor solution of BiI_3, (b) precursor deposition on the ITO/HTL substrate. The crystallization of BiI3 thin film by (c) thermal annealing (TA), (d) annealing the antisolvent (chlorobenzene (CB)) dripped film (AS), and (e) annealing under ambient solvent (CB or dimethylformamide (DMF)) vapor (CB or DMF-SVA).*

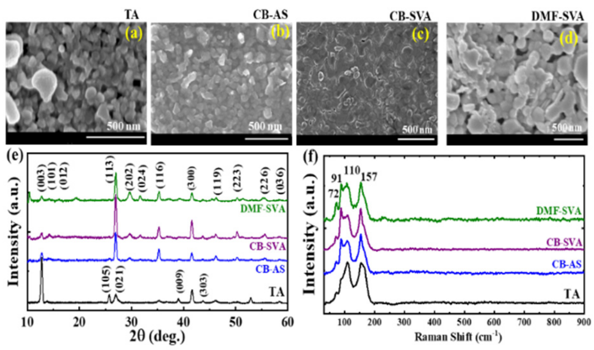

Fig. 5. *SEM images of the BiI_3 thin films crystallized via (a) TA, (b) CB-AS, (c) CB-SVA, (d) DMF-SVA. The characteristics of respective films (e) XRD patterns, and (f) Raman spectra.*

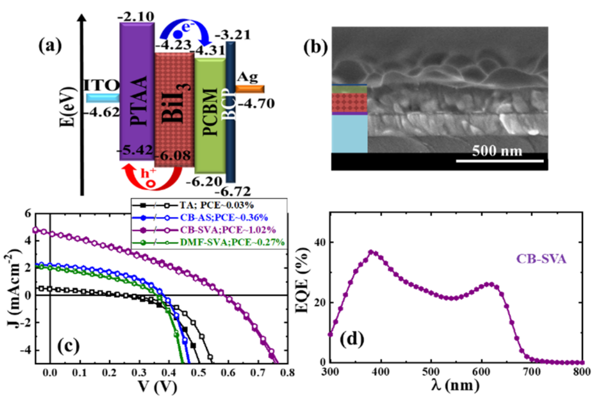

Fig. 6. *Schematic of the energy band diagram (a), cross-sectional image of BiI_3 based solar cells (b). J-V characteristics of BiI_3-based solar cells (c). External quantum efficiency (EQE) spectra (d) of the corresponding device with BiI_3 device with CB-SVA.*

conversion efficiency of ~1.02% with an open circuit voltage of 0.587 V. This is attributed to the improvement in film quality comprising uniform morphology, increase in grain size, and hence mitigation of defect profile. The spectral response of the best device is shown in Fig. 6d.

2. 発表（研究成果の発表）

"Research Paper"

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2. Dhruba B. Khadka, * Y. Shirai, M. Yanagida, K. Miyano, Mitigation of the Recombination Activities with Rubidium incorporation for Efficient and Stable FASnI3 Solar Cells, International Conference on Perovskite, Organic Photovoltaics and Optoelectronics (IPEROP)-2020, Tsukuba, Japan, Poster Presentation, 20th-22th Jan, (Japan, 2020).