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研究課題名（和文）Innovative reactive polyiodide melt method to fabricate lead-free Perovskite absorber layers and solar cells

研究課題名（英文）Innovative reactive polyiodide melt method to fabricate lead-free Perovskite absorber layers and solar cells

研究代表者
Ｋａｚａｏｕｉ　Ｓａｉｄ（KAZAOUI, SAID）

国立研究開発法人産業技術総合研究所・エネルギー・環境領域・主任研究員

研究者番号：３０３５６７６１

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研究成果の概要（和文）：本研究の目標は、独自のReactive Polyiodide Melt (RPM)法を用いて、新し鉛フリーペロブスカイト吸収層と太陽電池を探索することでした。最も重要な研究成果は、Sn金属薄膜とCH3NH3I(MAI)蒸気と反応させることでMASnI3 ペロブスカイトを製膜する方法を研究開発しました。更に、Bi-AgとMAI薄膜を作製した上でヨウ素(I2)蒸気と反応させることでAgBiI4膜を作製しました。AgBiI4膜を用いてFTO/TiO2/AgBiI4/spiro-OMeTAD/Au太陽電池を作製し、変換効率は約5%を達成しました。研究結果は国際会議で発表され、学術誌に掲載されました。

研究成果の学術的意義や社会的意義
Perovskite solar cells (PSCs) can overcome the energy and the environment issues of our society. However, the best PSCs contain Pb compounds, which are toxic and severely regulated. We implemented our original Reactive Polyiodide Melt (RPM) method to produce Pb-free materials based on Sn and Bi-Ag.

研究成果の概要（英文）：The goal of our project, using our original Reactive Polyiodide Melt (RPM) method (published in Nature Nanotechnology 14, 57 (2019)), was to explore new Pb-free absorber layers for solar cells (PSCs), in order to solve the problem of toxic Pb in Perovskite. The most important achievements are the synthesise of MASnI3 (CH3NH3PbI3)) perovskite by reacting Sn metal thin films with CH3NH3I (MAI) vapor. From the analysis of the XDR data, we suggested a direct conversion mechanism involving the thermal decomposition of MAI and the release of gases as follows Sn+3MAI→MASnI3+(2CH3NH2+H2). We think that this method can be extended to make FAPbI3. Furthermore, AgBiI4 films were prepared by making a stacked layer of Bi-Ag alloys and MAI thin film by vacuum process, and then exposing it to iodine (I2) vapor. The FTO/TiO2/AgBiI4/spiro-OMeTAD/Au solar cells were fabricated, and the best conversion efficiency was 5%. Our results were presented at international conferences and published in journals.

研究分野：エネルギー関連化学

キーワード：Perovskite　Photovoltaics　Solar cells　Pb free　Sn　Bi-Ag

１．研究開始当初の背景 Introduction

Perovskite solar cells (PSCs), which feature high efficiency and low manufacturing cost, are attracting the attention of academia and industry, since the pioneering studies by T. Miyasaka et al. (Toin Uni.,Japan). However, their commercialization might be hindered because PSCs contain lead (e.g. Pb, PbI_2), which are toxic and regulated.

２．研究の目的 Goals

Our research goals are to synthesize perovskite (or perovskite-like) absorber layers and to fabricate solar cells using non-toxic metals (such as Sn, Bi, Ag, Cu) based on our original “Reactive Polyiodide Melt”(RPM) method [1]. Furthermore, our goals are to elucidate the reaction mechanisms and oxidation states of these metals in perovskite (or perovskite-like) materials.

３．研究の方法 Methods

To achieve our goals, we implemented our original RPM method [1], to synthesize perovskite (or perovskite-like) materials by controlling the reaction between non-toxic metals (e.g. Sn, Bi, Ag) and CH_3NH_3I (MAI) vapor with or without additional exposure to iodine (I_2) vapor. Then, for the most promising materials, we fabricated the solar cells using the well-established architecture based on TiO_2 electron selective layer and spiro-OMeTAD hole selective layer. We analyzed the materials mainly by x-ray diffraction (XRD) and the solar cells by performing IV/EQE measurements.

4. 研究成果 Results

4.(1) Materials based on Sn

Sn-based PSCs are of great interest to overcome the problem of toxicity of Pb-based PSCs. Several methods to synthesize Sn-based perovskite films by solution and vacuum processes have already been reported. For instance, $CH_3NH_3SnI_3$ ($MASnI_3$) are often synthesized by the reaction of SnI_2 and CH_3NH_3I (MAI) dissolved in organic solutions including various additives to control the crystallinity and to prevent the oxidation of Sn^{2+} into Sn^{4+}, which are known to hamper the performance of the solar cells. Note that very few reports have also demonstrated that $CH_3NH_3SnI_3$ thin films can be synthesized by the reaction of Sn thin films in the presence of MAI in solution or in gas phase. Based on this information and on our previous experience with the synthesis of $CH_3NH_3PbI_3$ ($MAPbI_3$) by reaction of Pb thin film in the presence of $CH_3NH_3I+I_2$, we studied the synthesis of $CH_3NH_3SnI_3$ ($MASnI_3$) using Sn thin films and MAI powders.

We find that $CH_3NH_3SnI_3$ thin film can be readily synthesized by reaction of Sn thin film (substrate at 90°C, pre-deposited on glass subtract by vacuum deposition process) and CH_3NH_3I powder (heated at 145°C, 0.1 Atm) in a 2-zone furnace, as shown in figure 1. We observed that the synthesis of $CH_3NH_3SnI_3$ thin films occurred by a one-step chemical vapor reaction on Sn thin film in the presence of CH_3NH_3I molecules as well as their byproducts due to thermal decomposition. From the analysis of XRD (Figure 2(a), (b)), thermogravimetry and mass spectroscopy data, we discussed several reaction mechanisms, as described in eq. (1) and eq. (2). Note that the chemical nature of the intermediate phase and the byproducts could not be elucidated in this work.

$$Sn + 3CH_3NH_3I \rightarrow CH_3NH_3SnI_3 + (2CH_3NH_2 + H_2) \quad \text{eq.(1)}$$

$$Sn + 2CH_3NH_3I \rightarrow SnI_2 + 2CH_3NH_2 + H_2 \text{ then } SnI_2 + CH_3NH_3I \rightarrow CH_3NH_3SnI_3 \quad \text{eq.(2)}$$

Interestingly, the above-mentioned reaction paths do not require any additives (e. g. SnF_2, organic compounds) to prevent the formation of Sn^{4+}, because the reaction $Sn+Sn^{4+}\rightarrow 2Sn^{2+}$ will take place until all the Sn is completely consumed. We anticipate that our method can be applied to synthesize various types of Sn-based perovskite (e.g., $FASnI_3$), which can be more stable and efficient than $MASnI_3$. It should be noted that if the conditions were unoptimized (e.g. temperature of the Sn substrate and MAI source, ratio of Sn compared to MAI, pressure, etc.), then the reaction would lead to a mixture of $CH_3NH_3SnI_3$ ($MASnI_3$) including unreacted Sn and/or unreacted MAI, as shown in XRD spectra in figure 2(c).

Unfortunately, we did not fabricate Sn-based solar cells, because we decided to focus on exploring various materials, as described in the next sections. Note that using the Sn/MAI reaction (Fig. 1), Tavakoli et al. fabricated $TiO_2/CH_3NH_3SnI_3$/spiro-OMeTAD/Au solar cell and reported that the best power conversion efficiency was 4.6% [2].

We also attempted to synthesize $CH_3NH_3SnI_3$ ($MASnI_3$) by coating Sn thin film with MAI and subsequently exposing it to iodine vapor (I_2) as shown in eq. (3), in a very similar way as described in our previous work on Pb-based perovskite [1]. But we observed that the reaction always gave $(CH_3NH_3)_2SnI_6$ and SnI_4 (only consisting of Sn^{4+}) rather than the expected $CH_3NH_3SnI_3$ (only consisting of Sn^{2+}), because MAI+I_2 is a very strong oxidant compound (Figure 3). This is consistent with the fact that in Sn-based system Sn^{4+} is more stable than Sn^{2+}, in sharp contrast with Pb-based system where Pb^{2+} is the most stable one. This is a very important difference between Sn-based and Pb-based perovskite, which is one of the reasons why high purity and defect free Sn-based perovskite are still challenging to synthesize.

$$Sn + CH_3NH_3I + I_2 \rightarrow \text{(unelucidated intermediate phases)} \rightarrow (CH_3NH_3)_2SnI_6 + SnI_4 \quad \text{eq. (3)}$$

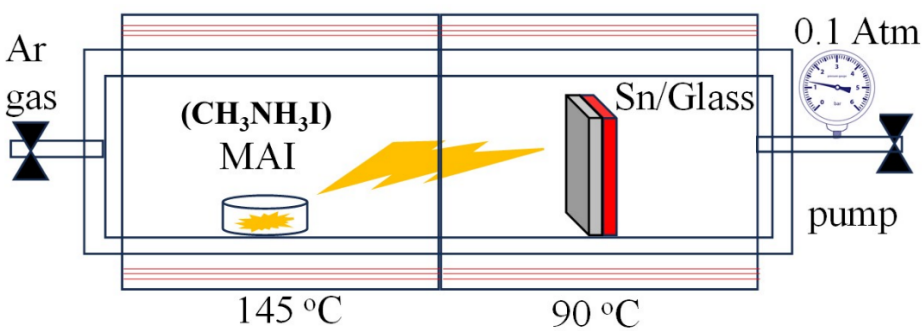

Figure 1: Experimental setup.

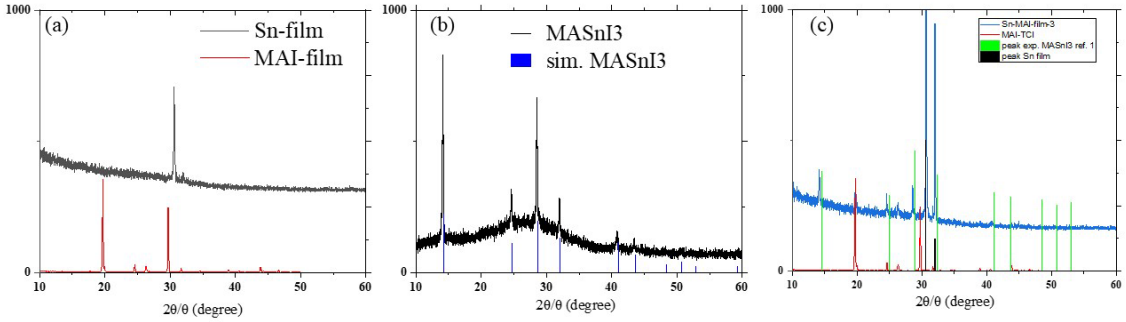

Figure 2: XRD spectra of (a) Sn and MAI films on glass before reaction; (b) $CH_3NH_3SnI_3$ ($MASnI_3$) film after reaction and simulation; (c) an incomplete reaction where Sn and MAI peaks are also identified.

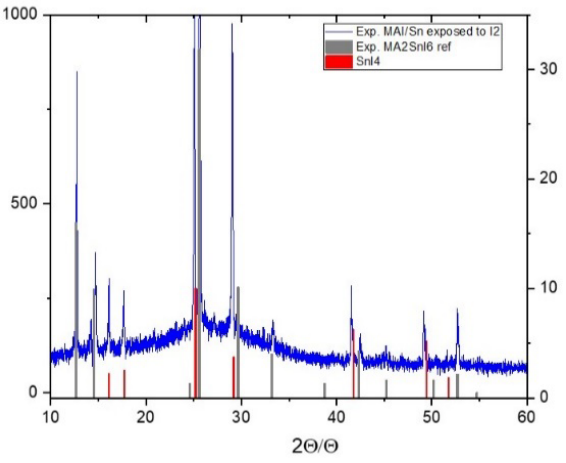

Figure 3: XRD spectra of $(CH_3NH_3)_2SnI_6 + SnI_4$

4.(2) Materials based on Ag-Bi alloys

Our RPM method can readily be applied to synthesize various types of perovskite-like materials from metals and alloys such as Bi and Ag-Bi, respectively. For instance, our preliminary results show that Bi thin film deposited on glass, then coated with MAI, and finally exposed to iodine (I_2) vapor gave Bi/3MAI + 3I_2 → $MA_3Bi_2I_9$. However, $MA_3Bi_2I_9$ consists of isolated face-shared Bi_2I_9 bioctahedra leading to zero-dimensional structures with poor transport properties and therefore unsuitable for solar cells.

To overcome this issue, we synthesized Ag-Bi alloys, as described in our publication [3]. We deposited a thin film of Ag-Bi alloy by co-evaporation of Ag and Bi metal (the targeted composition was $Ag_{0.5}Bi_{0.5}$ and thickness 40 nm), then we treated it with I_2 vapor (at 40°C) and finally we annealed it at 110°C to convert it $AgBiI_4$ film, as confirmed by XRD and EDX (Figure 4).

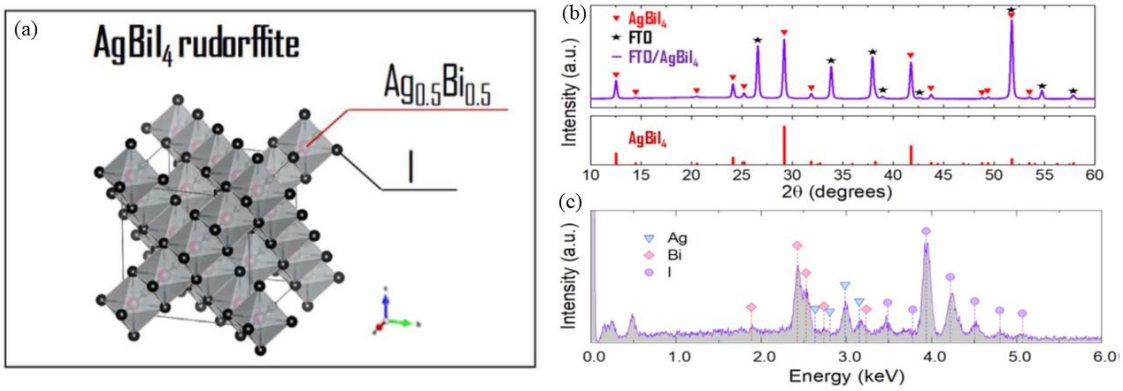

Figure 4: (a) Crystal structure of $AgBiI_4$. (b) XRD pattern of the $AgBiI_4$ film on FTO/glass substrate, and ICDD 04-012-2830 reference pattern for $AgBiI_4$. (c) EDX spectrum of the $AgBiI_4$ film. Reproduced from reference [3]

We fabricated the solar cells with the standard architecture TiO_2/$AgBiI_4$/spiro-OMeTAD/Au, as shown in figure 5. We studied their performance under LED light illumination and demonstrated a power conversion efficiency of 5% for an illumination of 1000 lux (here as an example, we intentionally focused on indoor application). Further studies are in progress for both indoor and outdoor applications.

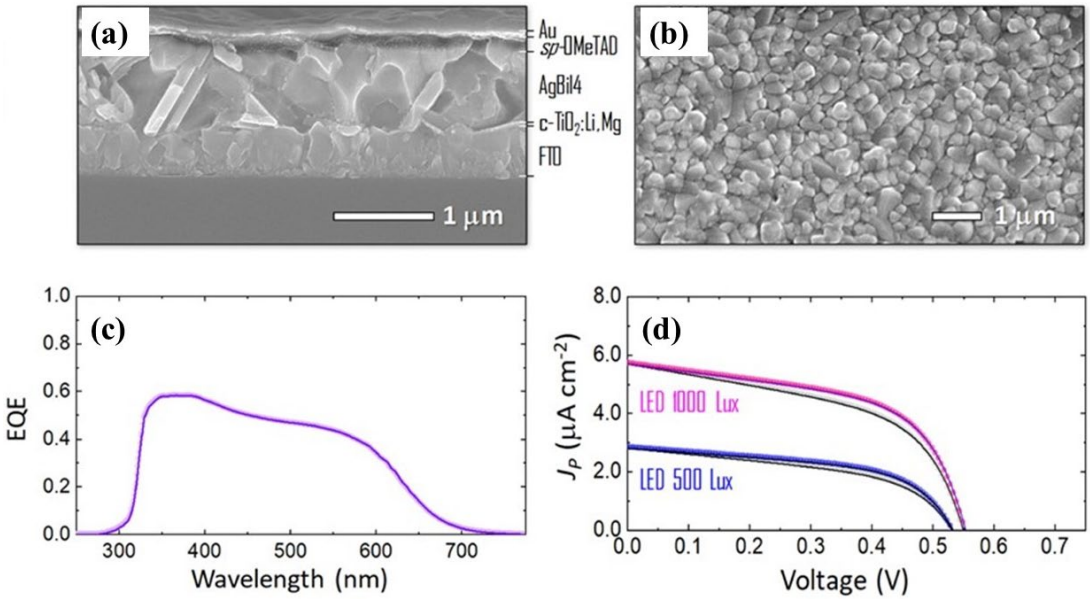

Figure 5: (a)SEM image of the cross section of $AgBiI_4$-based solar cell, (b) SEM image of the surface of $AgBiI_4$ film. (c) EQE and (d) IV curves of $AgBiI_4$-based solar cell. Reproduced from reference [3].

References:

[1] I. Turkevych, S. Kazaoui, et al., Nature Nanotechnology 14, 57 (2019)
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[2] M.M. Tavakoli, S.M. Zakeeruddin, M. Grätzel, Z. Fan, Adv. Mater. 30, 1705998 (2018)
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５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　2件／うちオープンアクセス　0件）

１．著者名 Turkevych Ivan、Kazaoui Said、Shirakawa Naoki、Fukuda Nobuko	４．巻 60
２．論文標題 Potential of AgBiI4 rudorffites for indoor photovoltaic energy harvesters in autonomous environmental nanosensors	５．発行年 2021年
３．雑誌名 Japanese Journal of Applied Physics	６．最初と最後の頁 SCCE06～SCCE06
掲載論文のDOI（デジタルオブジェクト識別子） 10.35848/1347-4065/abf2a5	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Chowdhury Towhid H.、Kayesh Md. Emrul、Lee Jae-Joon、Matsushita Yoshitaka、Kazaoui Said、Islam Ashraful	４．巻 3
２．論文標題 Post‐Deposition Vapor Annealing Enables Fabrication of 1 cm2 Lead‐Free Perovskite Solar Cells	５．発行年 2019年
３．雑誌名 Solar RRL	６．最初と最後の頁 1~4
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/solr.201900245	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計2件（うち招待講演　0件／うち国際学会　2件）

１．発表者名 Kazaoui Said
２．発表標題 Synthesis of MASnI3 Perovskite films by reaction of Sn metallic film with MAI vapor
３．学会等名 PEROP23 Asia-Pacific International Conference on Perovskite, Organic Photovoltaics and Optoelectronics（国際学会）
４．発表年 2022年

１．発表者名 Kazaoui Said
２．発表標題 MASnI3 perovskite films synthesized using Sn metallic thin films in presence of MAI vapor
３．学会等名 PEROP24 Asia-Pacific International Conference on Perovskite, Organic Photovoltaics and Optoelectronics（国際学会）
４．発表年 2023年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関