Effects of NH_4Cl addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic devices

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Effects of NH_4Cl addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solutions on photovoltaic properties were investigated. $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ -based photovoltaic devices were fabricated by a spin-coating technique, and the microstructures of the devices were investigated by X-ray diffraction and scanning electron microscopy. Current density–voltage characteristics were improved by a small amount of Cl-doping, which resulted in improvement of the efficiencies of the devices. The structure analysis indicated formation of a homogeneous microstructure by NH_4Cl addition to the perovskite phase, and formation of PbI_2 was suppressed by the NH_4Cl addition.

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1. Introduction

Perovskite-type methylammonium trihalogenoplumbates (II) ($\text{CH}_3\text{NH}_3\text{PbI}_3$, MAPbI_3) solar cells have been extensively studied owing to its easy fabrication process and the high conversion efficiencies compared to the common organic solar cells.^{1)–4)} After a conversion efficiency reached 15% in 2013,⁵⁾ higher efficiencies have been achieved for various device structures and processes,^{6,7)} and the conversion efficiency increased above 20%.^{8)–11)}

The photovoltaic properties of the perovskite solar cells are fairly dependent on compositions and the crystal structures of the perovskite compounds. Halogen atom doping, such as bromine (Br) or chlorine (Cl), at the iodine (I) sites of the perovskite crystals have been investigated.^{12)–15)} The doped Cl ions could lengthen the diffusion length of excitons, which resulted in the improvement in the conversion efficiency.^{12,15)} In our previous work,¹⁶⁾ PbCl_2 were added to the $\text{CH}_3\text{NH}_3\text{PbI}_3$, which resulted in the improvement $\text{CH}_3\text{NH}_3\text{PbI}_3$, and the highest conversion efficiency was obtained for the $\text{CH}_3\text{NH}_3\text{PbI}_{2.88}\text{Cl}_{0.12}$ cell.

In addition, studies on metal atom doping, such as tin (Sn),¹⁷⁾ germanium (Ge),^{18,19)} antimony (Sb),^{20,21)} arsenic (As),²²⁾ or thallium (Tl)¹⁹⁾ at the lead (Pb) sites have been performed. The optical absorption ranges of the perovskite solar cells were expanded by Sn or Tl-doping,^{17,19)} and the photoconversion efficiencies were improved by Sb-doping.^{20,21)} Further doping of cesium or formamidinium ($\text{NH}=\text{CHNH}_3$, FA) also improved the conversion efficiencies of the perovskite solar cells.⁹⁾ Detailed studies on the halogen, metal and/or FA doping at the I, Pb and/or CH_3NH_3 sites are intriguing for effects on the photovoltaic properties and microstructures.

The purpose of the present work is to investigate photovoltaic properties and microstructures of perovskite-type $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic devices, which were prepared by a spin-coating technique in air. The Cl element is expected to increase

the carrier diffusion length in the perovskite crystals,^{12,15)} and an improvement of the morphology and crystallinity of the thin films is also expected by adding NH_4Cl .^{23,24)} The effects of NH_4Cl addition using a mixture solution of perovskite compounds on the photovoltaic properties and microstructures were investigated by light-induced current density–voltage (J – V) characteristics, incident photon-to-current conversion efficiency (IPCE), X-ray diffraction (XRD), and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS).

2. Experimental procedures

A schematic illustration for the fabrication of the present $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic cells is shown in **Fig. 1**. The details of the fabrication process are described in the reported papers,^{5,16,20,25,26)} except for NH_4Cl . F-doped tin oxide (FTO) substrates were cleaned using an ultrasonic bath with acetone and methanol, and dried under nitrogen gas. 0.15 and 0.30 M TiO_2 precursor solution was prepared from titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, 0.055 and 0.11 mL) with 1-butanol (1 mL), and the 0.15 M TiO_2 precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s, and annealed at 125°C for 5 min. Then, the 0.30 M TiO_2 precursor solution was spin-coated on the TiO_x layer at 3000 rpm for 30 s, and annealed at 125°C for 5 min. This process of 0.30 M solution was performed two times, and the FTO substrate was sintered at 500°C for 30 min to form the compact TiO_2 layer. After that, TiO_2 paste was coated on the substrate by spin-coating at 5000 rpm for 30 s. For the mesoporous TiO_2 layer, the TiO_2 paste was prepared with TiO_2 powder (Nippon Aerosil, P-25) with poly(ethylene glycol) (Nacalai Tesque, PEG #20000) in ultrapure water. The solution was mixed with acetylacetone (Wako Pure Chemical Industries, 10 μL) and triton X-100 (Sigma-Aldrich, 5 μL) for 30 min, and was left for 12 h to suppress the bubbles in the solution. The cells were annealed at 120°C for 5 min and at 500°C for 30 min to form the mesoporous TiO_2 layer.²⁷⁾ For the preparation of the perovskite compounds, a solution of $\text{CH}_3\text{NH}_3\text{I}$ (Showa Chemical Co., Ltd., 98.8 mg), PbI_2 (Sigma-Aldrich, 289.3 mg), and NH_4Cl (Wako Pure Chemicals Industries, Ltd.,) was prepared with a

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Fig. 1. Schematic illustration for the fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic cells.

Table 1. Preparation composition of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells with NH_4Cl additive

Preparation composition	Amount of NH_4Cl additive (mg)
$\text{CH}_3\text{NH}_3\text{PbI}_3$	0
$\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{0.15}$	5
$\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{0.45}$	15
$\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{0.75}$	25
$\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{1.05}$	35
$\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{1.35}$	45

desired mole ratio in mixture of N,N -dimethylformamide (DMF, Nacalai Tesque, 225 μL) and γ -butyrolactone (Nacalai Tesque, 275 μL) at 60°C. Addition of the DMF to γ -butyrolactone is expected to improve the photovoltaic properties.^{23),24),28)} The preparation compositions of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells with a NH_4Cl additive are listed in **Table 1**. The solution of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ was introduced into the TiO_2 mesopores by a spin-coating method and annealed at 100°C for 15 min. Then, a hole transport layer (HTL) was prepared by spin-coating. For the hole transport layer, a solution of 2,2',7,7'-tetrakis[N,N -di(p-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, Wako Pure Chemical Industries, 36.1 mg) in chlorobenzene (Wako Pure Chemical Industries, 0.5 mL) was mixed with a solution of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, Tokyo Chemical Industry, 260 mg) in acetonitrile (Nacalai Tesque, 0.5 mL) for 12 h. The former solution with 4-tert-butylpyridine (Aldrich, 14.4 μL) was mixed with the Li-TFSI solution (8.8 μL) for 30 min at 70°C. All procedures for preparation of the thin films were performed in ordinary air. Lastly, gold (Au) contacts were evaporated as top metal electrodes. Layered structures of the present solar cells were denoted as $\text{FTO}/\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})/\text{spiro-OMeTAD}/\text{Au}$, as shown in Fig. 1.

J - V characteristics of the photovoltaic cells were measured under illumination at 100 mW cm^{-2} by using an AM 1.5 solar simulator (San-ei Electric, XES-301S). The solar cells were

Fig. 2. J - V characteristic of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ photovoltaic cells added with NH_4Cl .

Table 2. Measured photovoltaic parameters (top and average) of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_x$ cells

NH_4Cl (mg)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η_{max} (%)	η_{ave} (%)
0	16.8	0.870	0.482	7.05	6.66
5	18.0	0.886	0.488	7.78	6.54
15	20.0	0.903	0.504	9.10	8.91
25	21.4	0.909	0.492	9.58	9.22
30	19.6	0.894	0.540	9.46	9.16
35	19.9	0.903	0.536	9.63	9.10
40	19.4	0.863	0.516	8.64	8.40
45	17.1	0.885	0.539	8.16	8.08

illuminated through the side of the FTO substrates, and the illuminated area was 0.090 cm^2 . The IPCE of the cells were also measured (Enli Technology, QE-R). The microstructures of the thin film devices were investigated by using an X-ray diffractometer (Bruker, D2 PHASER), and a scanning electron microscope (Jeol, JSM-6010PLUS/LA) equipped with EDS.

3. Results and discussion

The J - V characteristics of the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})/\text{spiro-OMeTAD}$ photovoltaic cells under illumination are shown in **Fig. 2**, which indicates an effect NH_4Cl addition to the $\text{CH}_3\text{NH}_3\text{PbI}_3$. The measured photovoltaic parameters of the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells are summarized in **Table 2**. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ cell provided the highest power conversion efficiency (η_{max}) of 7.05%, and the averaged efficiency (η_{ave}) of three electrodes on the cells is 6.66%, as listed in Table 2. A short-circuit current density (J_{SC}) increased up to 21.4 mA cm^{-2} by an addition of 25 mg NH_4Cl , which would indicate an increase of carrier diffusion length. The highest efficiency was obtained for a cell added with 35 mg NH_4Cl , which provided the η_{max} of 9.63%, a fill factor (FF) of 0.536, a J_{SC} of 19.9 mA cm^{-2} , and an open-circuit voltage (V_{OC}) of 0.903 V. The highest average-efficiency was obtained for a cell added with 25 mg NH_4Cl , which provided an η_{ave} of 9.22%.

IPCE spectra of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells added with 30 mg NH_4Cl are shown in **Fig. 3**. The $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ device shows photoconversion efficiencies between 300 and 800 nm, which corresponds to an energy gap of 1.55 eV for the $\text{CH}_3\text{NH}_3\text{PbI}_3$. The IPCE was improved in the range of 450–

Fig. 3. IPCE spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells. Fig. 4. XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells.

750 nm by the addition of NH_4Cl to the $\text{CH}_3\text{NH}_3\text{PbI}_3$. In the present work, the energy gaps of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ phase were almost constant even by the Cl-doping, which agreed well with the constant values of the open-circuit voltages.

XRD patterns of $\text{FTO}/\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ devices are shown in Fig. 4. The diffraction peaks can be indexed by a cubic crystal system ($Pm\bar{3}m$) for the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ thin films. In addition to XRD peaks of the ordinary perovskite structure,

Fig. 5. (a) SEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Elemental mapping images of (b) Pb M line, (c) I L line, (d) C K line, and (e) N K line.

broader diffraction peaks due to the PbI_2 compound appeared in the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ film, as shown in Fig. 4. However, the NH_4Cl addition suppressed the formation of PbI_2 , and peak intensities of 100 of the perovskite phase increased.

The photovoltaic property of the non-annealed cell had been measured in the previous work.²⁵⁾ Although the PbI_2 compound was formed during annealing at 100°C , the perovskite structures changed from tetragonal into cubic phase, which resulted in the improvement of photovoltaic properties.

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals have a perovskite structure, and both I ions and CH_3NH_3 ions are disordered, which results in the disordered cubic structure.^{29,30)} For the as-deposited $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film, only XRD peaks of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were observed, and no XRD peak of PbI_2 was observed.²⁵⁾ After annealing at 100°C for 15 min, the unit cell volume decreased and an XRD peak of PbI_2 appeared,²⁵⁾ which indicated partial separation of PbI_2 from $\text{CH}_3\text{NH}_3\text{PbI}_3$. The XRD result of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in Fig. 4 also showed the existence of PbI_2 after annealing at 100°C for 15 min. This would indicate partial separation of PbI_2 from $\text{CH}_3\text{NH}_3\text{PbI}_3$ after annealing, and the formation of PbI_2 was suppressed by the NH_4Cl addition, which would result in the increase of conversion efficiencies of the devices.

A SEM image of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ cell without NH_4Cl is shown in Fig. 5(a). Perovskite crystals with sizes of 5–10 μm are observed at the surface of the mesoporous TiO_2 , and the crystals have a star-like shape. Elemental mapping images of Pb, I, C, and N by SEM-EDS are shown in Figs. 5(b)–5(e), respectively. The elemental mapping images indicate the particles observed in Fig. 5(a) correspond to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ compound. The composition ratios of elements Pb, I, and C:N were calculated from the EDS spectrum using background correction by normaliz-

Table 3. Measured compositions of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cells

NH_4Cl (mg)	Pb (at.%)	I (at.%)	Cl (at.%)	C:N (at.%)
0	34.8	65.2	—	57.1:42.9
5	33.5	61.8	4.7	52.0:48.0
15	32.4	62.6	5.0	54.7:45.3
25	32.2	62.5	5.3	54.9:45.1
35	34.2	58.1	7.7	54.7:45.3
45	33.5	58.2	8.3	54.2:45.8

Fig. 6. (a) SEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell with NH_4Cl additive of 5 mg. Elemental mapping images of (b) Pb M line, (c) I L line, (d) Cl L line, (e) C K line, and (f) N K line.

ing the spectrum peaks, as listed in Table 3. This result indicates that I might be deficient from the starting composition of $\text{CH}_3\text{NH}_3\text{PbI}_3$, and the deficient I might increase the hole concentration. In addition, carbon atoms are dispersed in the matrix.

Figure 6(a) is a SEM image of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell with 5 mg NH_4Cl additive. The surface morphology was drastically changed by the addition of NH_4Cl to the $\text{CH}_3\text{NH}_3\text{PbI}_3$. The particle sizes are a few μm , and the crystals have a round shape. The composition ratios of metal elements and C:N were calculated from the EDS spectrum, as listed in Table 3, which indicates that I might be deficient from the starting composition of $\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{0.15}$. On the other hands, Cl element would be appropriately doped in the $\text{CH}_3\text{NH}_3\text{PbI}_3$, as listed in Table 3. In Fig. 6(e), carbon atoms seems to be dispersed homogeneously.

Figure 7(a) is a SEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell added with 25 mg NH_4Cl . By adding 25 mg NH_4Cl to the $\text{CH}_3\text{NH}_3\text{PbI}_3$, the surface morphology was extremely changed, and no special crystal shape is observed, which would be due to an effect of NH_4Cl addition. Elemental mapping images of Pb M line, I L

Fig. 7. (a) SEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell with NH_4Cl additive of 25 mg. Elemental mapping images of (b) Pb M line, (c) I L line, (d) Cl L line, (e) C K line, and (f) N K line.

line, Cl K line, C K line, and N K line are shown in Figs. 7(b)–7(f), respectively, and the images indicate the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase is dispersed homogeneously on the photovoltaic device. These homogeneous surface structures would improve the photovoltaic properties. From the SEM-EDS results, site occupancies of I atom would also be less than 1, which might be due to the partial separation of PbI_2 from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase. The composition of NH_3 also seem to be deficient compared with that of the CH_3 , and it became almost constant by the NH_4Cl addition, which would indicate the NH_3 are doped at the vacant NH_3 positions.

Three assumed mechanisms could be considered for the increase of the photoconversion efficiencies. The first mechanism is as follows: when a small amount of Cl was doped in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase, diffusion length of excitons would be lengthened by the doped Cl atoms,^{12),15)} which would result in the increase of the J_{SC} values. The second is as follows: the homogeneous surface and interfacial structures formed by adding NH_4Cl to the $\text{CH}_3\text{NH}_3\text{PbI}_3$, which improved the photovoltaic properties, especially the FF values. The third is as follows: the deficient NH_3 positions are filled with NH_3 from NH_4Cl , which would lead to the stable perovskite structure by suppression of PbI_2 separation. Further studies are mandatory for precise structure determination of the devices.

The photovoltaic performance of the cell containing more than 35 mg was deteriorated, as listed in Table 2. This would be due to increase of series resistance by the remained undoped Cl element in the perovskite phase and undetermined compounds, which were observed as small XRD peaks around 22 and 32.5° for NH_4Cl 45 mg added sample in Fig. 4.

4. Conclusion

The effects of NH_4Cl addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solutions on photovoltaic properties were investigated. $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ -based photovoltaic devices were fabricated, and the microstructures of the devices were investigated by XRD and SEM-EDS. J - V characteristics and IPCE were improved by the NH_4Cl addition to perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solutions. The structural analysis also indicated the formation of a homogeneous microstructure by NH_4Cl addition, which improved the FF values and photoconversion efficiencies. The IPCE spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ cell was also improved by the NH_4Cl addition, and showed effective carrier-generation in the range of 300 and 800 nm.

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References

- 1) A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, **131**, 6050–6051 (2009).
- 2) J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, *Nanoscale*, **3**, 4088–4093 (2011).
- 3) H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel and N.-G. Park, *Sci. Rep.*, **2**, 591 (2012).
- 4) M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, **338**, 643–647 (2012).
- 5) J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, **499**, 316–320 (2013).
- 6) K. Wojciechowski, M. Saliba, T. Leijtens, A. Abate and H. J. Snaith, *Energy Environ. Sci.*, **7**, 1142–1147 (2014).
- 7) H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, **345**, 542–546 (2014).
- 8) W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Science*, **348**, 1234–1237 (2015).
- 9) M. Saliba, T. Matsui, J. Y. Seo, K. Domanski, J. P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.*, **9**, 1989–1997 (2016).
- 10) M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J. P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K. H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel and M. K. Nazeeruddin, *Nat. Energy*, **1**, 15017 (2016).
- 11) D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J. P. C. Baena, J. D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Sci. Adv.*, **2**, 1501170 (2016).
- 12) D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent and O. M. Bakr, *Science*, **347**, 519–522 (2015).
- 13) S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, **342**, 341–344 (2013).
- 14) W. Nie, H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H. L. Wang and A. D. Mohite, *Science*, **347**, 522–525 (2015).
- 15) Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, **347**, 967–970 (2015).
- 16) T. Oku, K. Suzuki and A. Suzuki, *J. Ceram. Soc. Japan*, **124**, 234–238 (2016).
- 17) F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang and M. G. Kanatzidis, *Nat. Photonics*, **8**, 489–494 (2014).
- 18) T. Krishnamoorthy, H. Ding, C. Yan, W. L. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M. Asta, N. Mathews and S. G. Mhaisalkar, *J. Mater. Chem. A Mater. Energy Sustain.*, **3**, 23829–23832 (2015).
- 19) Y. Ohishi, T. Oku and A. Suzuki, *AIP Conf. Proc.*, **1709**, 020020 (2016).
- 20) T. Oku, Y. Ohishi and A. Suzuki, *Chem. Lett.*, **45**, 134–136 (2016).
- 21) T. Oku, Y. Ohishi, A. Suzuki and Y. Miyazawa, *Metals (Basel)*, **6**, 147 (2016).
- 22) A. Hamatani, Y. Shirahata, Y. Ohishi, M. Fukaya and T. Oku, *Adv. Mater. Phys. Chem.*, **7**, 1–10 (2017).
- 23) C. Zuo and L. Ding, *Nanoscale*, **6**, 9935–9938 (2014).
- 24) J. He and T. Chen, *J. Mater. Chem. A Mater. Energy Sustain.*, **3**, 18514–18520 (2015).
- 25) T. Oku, M. Zushi, Y. Imanishi, A. Suzuki and K. Suzuki, *Appl. Phys. Express*, **7**, 121601 (2014).
- 26) M. Zushi, A. Suzuki, T. Akiyama and T. Oku, *Chem. Lett.*, **43**, 916–918 (2014).
- 27) T. Oku, N. Kakuta, K. Kobayashi, A. Suzuki and K. Kikuchi, *Prog. Nat. Sci.*, **21**, 122–126 (2011).
- 28) H. B. Kim, H. Choi, J. Jeong, S. Kim, B. Walker, S. Song and J. Y. Kim, *Nanoscale*, **6**, 6679–6683 (2014).
- 29) H. Mashiyama, Y. Kurihara and T. Azetsu, *J. Korean Phys. Soc.*, **32**, S156–S158 (1998).
- 30) Y. Kawamura, H. Mashiyama and K. Hasebe, *J. Phys. Soc. Jpn.*, **71**, 1694–1697 (2002).