Investigating the feasibility of symmetric guanidinium based plumbate perovskites in prototype solar cell devices

Kulkarni, Sneha Avinash; Baikie, Tom; Muduli, Subas; Potter, Rob; Chen, Shi; Yanan, Fanan; Bishop, Peter; Lim, Swee Sien; Sum, Tze Chien; Mathews, Nripan; White, Tim J.

2017

Kulkarni, S. A., Baikie, T., Muduli, S., Potter, R., Chen, S., Yanan, F., . . . White, T. J. (2017). Investigating the feasibility of symmetric guanidinium based plumbate perovskites in prototype solar cell devices. *Japanese Journal of Applied Physics*, 56(8), 08MC05-. doi:10.7567/jjap.56.08mc05

<https://hdl.handle.net/10356/141483>

<https://doi.org/10.7567/JJAP.56.08MC05>

© 2017 The Japan Society of Applied Physics. All rights reserved. This paper was published in *Japanese Journal of Applied Physics* and is made available with permission of The Japan Society of Applied Physics.

Downloaded on 26 Apr 2023 16:56:14 SGT

Investigating the feasibility of symmetric guanidinium based plumbate perovskites in prototype solar cell devices

Sneha A. Kulkarni^{1*}, Tom Baikie¹, Subas Muduli¹, Rob Potter², Shi Chen⁴, Fanan Yanan³, Peter Bishop², Swee Sien Lim⁴, Tze Chien Sum⁴, Nripan Mathews^{1,3*}, and Tim J. White³

¹Energy Research Institute@NTU (ERI@N), Nanyang Technological University, Singapore 637553

²Catalyst and Materials department, Johnson Matthey Technology Centre, Sonning Common, Reading RG4 9NH, U.K.

³School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798

⁴Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

*E-mail: sakulkarni@ntu.edu.sg; Nripan@ntu.edu.sg

Abstract: In this work we have studied the feasibility of highly symmetric guanidinium (GA; CH_6N_3) cation in perovskite based solar cells. It is an alternative to the methyl ammonium (MA; CH_3NH_3) or formamidinium (FA; $\text{CH}(\text{NH}_2)$) ions commonly utilized in the perovskite solar cells, may bring additional advantages due to its triad rotational symmetry and zero dipole moment (μ). We noticed that due to steric factors, GA preferably forms two-dimensional (2D) layer, where GA_2PbI_4 is favored monoclinic structure ($E_g = 2.5$ eV) and the obtained device efficiency is $\eta = 0.45\%$. This study provides a guideline for designing guanidinium based perovskite absorbers for solar cell devices. In addition, through further compositional engineering with mixed organic cations using GA may enhance the device performance. © 2017 The Japan Society of Applied Physics

Introduction

Organic–inorganic hybrid perovskites (ABX_3) show promise as low-cost materials in high performance optoelectronics^{1–3} and shown a remarkable improvements in power conversion efficiency (PCE) from 3.8% to in excess of 22.1%.^{4–10} Moreover, the optical and electronic properties of hybrid perovskites can be tuned by varying the proportions of inter-framework species [$\text{A} = \text{Cs}=\text{methyl ammonium (MA)}=\text{formamidinium (FA)}$], framework cations ($\text{B} = \text{Pb}=\text{Sn}$) and halides ($\text{X} = \text{I}=\text{Br}=\text{Cl}$).^{5,6,11–14} Strategies to enhance performance including solvent processing,⁸ compositional engineering^{7,14,15} and various device architecture have met with mixed success and reproducibility. Key challenge is the development of compositions with higher thermal and ambient stability that avoid toxic elements.^{16–18} Typically, when evaluating metal ion replacements for Pb with Sn=Ge, only MA=FA=Cs are considered for the A site. Recently, Giorgi et al.¹⁹ used density functional theory (DFT) to predict that three-dimensional (3D) guanidinium (GA) lead iodide perovskites (GAPbI_3), and formadinium–guanidinium ($\text{FA}_{1-x}\text{GA}_x\text{PbI}_3$) intermediate compounds, will show enhanced thermodynamic stability, lower formation energy, and a narrower bandgap –1.49 eV for GAPbI_3 as compared to 1.56 eV for MAPbI_3 . Although the existence of 3D GAPbI_3 remains speculative, such properties, if proven experimentally, would make this phase a superior photovoltaic material with reduced current voltage hysteresis. In guanidinium, the carbon is surrounded by three NH_2 groups in C_{3v} or D_{3h} site symmetry.²⁰ The three NH_2 groups increase bonding between the negatively charged (δ^-) I atom and positively charged (δ^+) ammonium H atom, thereby modifying the structural and electronic properties of GA perovskite compared to the MABX_3 and FABX_3 chemical analogues (Fig. 1). Furthermore, GA also opens opportunities to develop novel device architectures with higher efficiency and pronounced stability in non-plumbate perovskite systems. For example, GA bearing frameworks have been reported for multiferroic applications.²¹ The tolerance factor (τ), widely used for crystallochemical analogues of 3D perovskites has been extended to hybrid analogues.²² The size of $\text{GA}^+ = 2.78$ Å (ionic radius), in GAPbI_3 leads to $\tau > 1$ ($\tau = 1.03$), indicating it is marginally large to be incorporated into the cavity formed by the corner-connected PbI_6 octahedra. In comparison MA (2.17 Å) and FA (2.53 Å) yield $\tau = 0.912$ and $\tau = 0.987$ in the 3D MAPbI_3 and FAPbI_3 perovskites (Fig. 1). Previous reports of 3D GAPbI_3 formation remain ambiguous, whereas the existence of 2D GA_2PbI_4 perovskite is unequivocal.^{20,23,24} Here, the synthesis and characterization of GA based perovskites are reported in polycrystalline powder as well as thin-film forms. The GA-perovskites were formed by mixing the guanidinium iodide (GAI): lead iodide (PbI_2) in 1 : 1 (designated as GAPbI_3) and 2 : 1 (designated as GA_2PbI_4) mole ratio. Powder X-ray diffraction (XRD), optical absorption spectroscopy, field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), ultraviolet (UV) photoelectron spectroscopy (UPS), and time-resolved and steady-state photoluminescence (PL) measurements were conducted. In addition, prototype solar cells were fabricated using GAPbI_3 and GA_2PbI_4 absorber materials.

Fig. 1. (Color online) The structural representation of MA, FA, and GA cation along with the tolerance factor of corresponding perovskite with respect to effective ionic radius, $\text{Pb}^{2+} = 1.19 \text{ \AA}$, $\text{I}^- = 2.2 \text{ \AA}$, $\text{MA} = 2.17 \text{ \AA}$, $\text{FA} = 2.53 \text{ \AA}$, and $\text{GA} = 2.78 \text{ \AA}$: carbon — red, nitrogen — blue, and hydrogen — grey.

1. Experimental methods

1.1 Perovskite precursor solution preparation of GAPbI₃ and GA₂PbI₄: The guanidinium iodide [$\text{C}(\text{NH}_2)_3\text{I}$; Dyesol] and lead iodide (PbI_2 ; Alfa Aesar) were added into dimethylformamide (DMF) in 1 : 1 and 2 : 1 mole ratio in order to prepare GAPbI₃ and GA₂PbI₄ respectively. These solutions were stirred at 70 °C for 8–10 h. The perovskite films are prepared by spin coating the solution at 2500 rpm for 30 s on fluorine-doped tin oxide (FTO)= blocking layer (BL) TiO₂=mesoporous TiO₂ substrate. Thus, prepared substrates were used for all further characterizations. In order to prepare the powder precursors, we have followed the two approaches. In first approach, the above made precursor solution in DMF was drop casted on the cleaned glass substrate and subsequently annealed at 130 °C in order to evaporate the solvent inside the glove box. In second approach, the powders were made using [$\text{C}(\text{NH}_2)_3\text{I}$] and lead acetate [$\text{Pb}(\text{CH}_3\text{CO}_2)_2$] precursors in DMF in stoichiometric ratios and also annealed at 130 °C.

1.2 Material characterization

Top view and cross sectional images of perovskite films and solar cells were recorded using a FESEM (JEOL JSM-7600F, 5 kV). Photocurrent–voltage (I – V) measurements were carried out using San-Ei Electric XEC-301S under AM 1.5 G. UV–visible absorption spectra were collected with a Shimadzu UV3600 spectrophotometer. Structural and phase characterization of the as-prepared film was achieved by XRD. The XRD patterns were recorded using Bruker AXS D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) from 10 to 70° 2 θ . The UPS were performed with a He I (21.2 eV) source and an electron analyser (Omicron EA125). TGA for GAPbI₃ and GA₂PbI₄ perovskite were carried out using TA Instruments TGA 500 from RT to 900 °C in nitrogen atmosphere at heating rate of 100 °C/min. The fundamental 800 nm output of a Coherent Libra™ regenerative amplifier (50 fs, 1 kHz, 800 nm) was frequency- doubled to 400 nm to generate the excitation beam for optical spectroscopy. The excitation pulse is filtered to eliminate the fundamental 800 nm wavelength. Time-resolved and steady- state PL were performed in a backscattering geometry at an angle of ~150° by a collimating lens pair. For steady-state PL, the emission was collected by a fibre coupled to an Acton Spectra Pro 2500i spectrometer with a Princeton Instruments PIXIS 400B CCD camera. For time-resolved PL, the emission was collected by an Acton Spectra Pro 2300i monochromator coupled to an Optronis Optoscope™ streak camera, which has a temporal resolution of ~10 ps. An Ultrafast Systems HELIOS femtosecond transient absorption spectrometer was used for femtosecond pump–probe experiments, using a pump wavelength of 400 nm and a white-light continuum probe generated by the fundamental 800 nm pulse through a CaF₂ crystal. The white-light continuum was filtered by a blue-green bandpass filter to eliminate the fundamental 800 nm wavelength.

1.3 Device fabrication

Preparation of TiO₂ substrates: FTO glass substrates were laser etched to form the desired pattern. Subsequently, the substrates were cleaned with decon soap, deionized (DI) water and ethanol, 15 min for each cleaning cycle. A compact TiO₂ layer also known as blocking layer (80–100 nm) was deposited by aerosol spray-pyrolysis using a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt % in isopropanol) and absolute ethanol in a 1 : 9 ratio (v=v) at 450 °C using compressed air as a carrier gas. Subsequently, after cooling, these substrates were immersed in an aqueous solution 40 mM TiCl₄ for 30 min at 70 °C, followed by rinsing with DI water and ethanol. A mesoporous TiO₂ layer (~400 nm) composed of 20-nm-sized particles was then deposited by spin coating and subsequently annealed at 500 °C for 30 min. Preparation of GAPbI₃ and GA₂PbI₄ perovskite absorbers and film deposition were carried out as mentioned in Sect. 2.1. An organic hole conductor 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamined)9,9'-spiro- bifuorene (spiro-OMeTAD) was dissolved in chlorobenzene (100 mg/mL) and spin coated on these substrates. Additives like Li(CF₃SO₂)₂N (24.2 µL/mL from stock solution of 520 mg/mL), *tert*-butylpyridine (29 µL/mL) and FK102 dopant (24 µL, stock solution 300 mg/mL) were added to the above solution. Thus prepared (HTM) solution (40 µL) was spun coated on perovskite film at 4000 rpm at 30 s. Subsequently masked (shadow masking) substrates were placed in a thermal evaporator for gold (Au) deposition (~100 nm). The active area was defined by the overlap of TiO₂ and Au (0.2 cm²). During measurements, the samples were masked using a black tape, to prevent the stray currents generated away from the active area.

2. Results and discussion

2.1 XRD analysis

Figure 2 shows a Pawley fit of the powder XRD of pattern of GA based perovskites prepared by mixing GAI : PbI₂ in 1 : 1 (designated as GAPbI₃) and 2 : 1 (designated as GA₂PbI₄) mole ratio (details in supporting information). A Pawley fit of the XRD pattern of GA perovskite prepared using GAI : PbI₂ in 2 : 1 mole ratio was consistent with 2D GA₂PbI₄ perovskite with the reported monoclinic cell $P2_1/n$; 14 with lattice constants $a = 12.8540(12)$ Å, $b = 27.098(4)$ Å, $c = 9.311(2)$ Å, and $\beta = 90.75(2)$ Å [Figs. 2(a) and 2(e)].²⁵⁾

A single low intensity reflection at 15° 2θ, could not be assigned to any known Pb or I containing phase. As GA₂PbI₄ shows temperature-dependent polymorphism, this reflection may arise from a lower symmetry polymorph. Powder XRD of GA₂PbI₄ thin-films show intense *h*00 reflections indicative of texture with the Pb–I layers parallel to the substrate surface [Fig. 2(c)]. As already noted, although the synthesis of 3D GAPbI₃ has been reported,²⁴⁾ crystallographic confirmation is lacking, and attempts to prepare this compound using different starting materials proved unsuccessful (Fig. S1 supplementary data). However, the XRD pattern of one synthesis could be Pawley fitted to a hexagonal cell with $a = 18.3605(4)$ Å and $c = 10.9372(3)$ Å, with PbI₂ present as a minor second phase [Fig. 2(b)]. These cell constants would be consistent with a 1D perovskite containing face sharing PbI₆ octahedral columns, similar to FAPbI₃ [$a = 8.9920(9)$ Å

Fig. 2. (Color online) Pawley fit of the powder XRD pattern of (a) GA_2PbI_4 and (b) GAPbI_3 powders, (supplementary data), (c) GA_2PbI_4 and GAPbI_3 perovskite film prepared by spin coating on mesoporous TiO_2/FTO substrate (left side): Polyhedral representation of (d) 1D, (e) 2D, and (f) 3D perovskites, with examples of yellow — 1D, black — 3D polymorphs of FAPbI_3 and 2D GA_2PbI_4 perovskites. The details of the yellow — 1D and black — 3D polymorphs of FAPbI_3 demonstrated in earlier reports.^{27,28} The green polyhedra represent the PbI_6 octahedra with I atoms shown as orange spheres (right side).

and $c = 11.0139(7) \text{ \AA}$], but with a double a -cell edge.⁹ The prototypical 3D ABX_3 perovskite consists of corner sharing BX_6 octahedra with the “A” cation located in a BX_{12} cuboctahedron. The B–X bonds are strong, with the BX_6 octahedra approximated as rigid units. Therefore, the cuboctahedral cage creates an upper limit on A-cation size that can be accommodated in a given BX_6 framework. Accordingly, a Goldschmidt’s factor (τ) in the range 0.95–1.0 favours cubic structures, while $\tau < 0.95$ leads to octahedral tilting leading to tetragonal, orthorhombic, and monoclinic 3D varieties.²⁶ Alternatively, for relatively large A cations where $\tau > 1$, a material adopts the structure containing 1D hexagonal columns of face-sharing BX_6 octahedra¹³ [Fig. 2(d)], rather than a 3D network of corner linked octahedra [Fig. 2(f)]. At even larger “ τ ”, the 2D perovskites emerge [Fig. 2(e)]. The details of the yellow-1D and black- 3D polymorphs of FAPbI_3 demonstrated in earlier re- ports.^{27,28} Based on thermogravimetric analysis, and in

absence of crystallographic confirmation, GAPbI₃ is reported dimorphic, appearing as phase (II) (70 °C) and Phase (I) (170 °C). Phase (I) is apparently metastable at ambient conditions and partially converts to phase II over several hours.²³ In this study GAPbI₃ perovskite films annealed at 70 and 170 °C changed from yellow to orange after treating at the higher temperature (170 °C, N₂ atmosphere, 20 min), but returns to yellow on cooling as previously reported.²³ However, the XRD patterns did not change significantly (Fig. S2 supplementary data). Furthermore, GAPbI₃ compositions suggest the co-existence of orthorhombic and hexagonal polymorphs (at room temperature), however this was not supported through refinement. Further experimental work is in progress to determine whether the crystal structure of GAPbI₃ is a 3D framework or 1D columnar phase. Both the guanidinium plumbate compositions (GAPbI₃ and GA₂PbI₄) are yellow (insert photographs in Fig. 2), the in contrast to the experimentally derived value. Secondary electron images (SEI) of GAPbI₃ and GA₂PbI₄ deposited on the mesoporous TiO₂ substrate [Figs. 3(b) and 3(c)] show larger, aggregated crystallites for the latter. In contrast, for both powder samples rod-like morphology was observed (Fig. S4 supplementary data). These perovskites are stable up to 300 °C. Decomposition of the organic moiety begins at 305 °C and only PbI₂ is preserved above 400 °C absence of the characteristic lead iodide (PbI₂) XRD reflection at 12.50° (2θ) confirming the colour arises from the perovskites [Fig. 2 (c)].

Fig. 3. (Color online) (a) Optical absorption spectra, (b, c) FESEM images of the GAPbI₃ and GA₂PbI₄ perovskite films prepared by spin coating on mesoporous TiO₂/FTO substrate.

Table I. Characteristic photovoltaic parameters: J_{sc} , V_{oc} , FF, and η of the GAPbI₃ and GAPbI₄ devices under a simulated full sunlight of 100 mW cm⁻².

	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
GAPbI ₃	0.402	652	62.8	0.16
GA ₂ PbI ₄	1.28	642	55.0	0.45

2.2 UV-vis and FESEM measurements

The optical absorption (400–800 nm) spectra of GAPbI₃ and GA₂PbI₄, recorded from spin-coated films on polycrystalline TiO₂ substrates, yielded band gaps [tabulated as an insert of Fig. 3(a)] of approximately 2.52 eV (Fig. S3 supplementary data). However, this is much higher than for MAPbI₃ (1.56 eV) and FAPbI₃ (1.46 eV), suggesting GAPbI₃ is not a 3D polymorph; although a weak absorbance onset at 750 nm (1.65 eV) is evident.²⁹ Conversely, simulations that assume the existence of 3D GAPbI₃ predict a direct band of 1.49 eV, (Fig. S5 supplementary data a).

2.3 Device measurements

The characteristic current density–voltage (J – V) curves for the GAPbI₃ and GA₂PbI₄ devices are distinct [Fig. 4(a) and Table I]. The band energy levels of GAPbI₃ and GA₂PbI₄ determined by UPS and UV–vis measurements [Figs. 4(b) and S5 e supplementary data] align with TiO₂ and Spiro-OMeTAD energy levels, which are typical components for perovskite-based solar cell devices. The cells achieved short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and efficiency (η) for GAPbI₃, 0.402 mA/cm², 652 mV, 62.6%, 0.16% and for GA₂PbI₄ of 1.28 mA/cm², 642 mV, 55 and 0.45%, respectively.

Fig. 4. (Color online) (a) Characteristic current density vs voltage curves of the GAPbI₃ and GA₂PbI₄ perovskites under a simulated full sun illumination, device area 0.2 cm², (b) energy level band diagram calculated from the UPS measurements (Fig. S6 supplementary data), and the cross section FESEM images of (c) GAPbI₃ and (d) GA₂PbI₄ perovskite based devices.

The poor performance of GAPbI₃ is consistent with a 1D structure similar to that found in perovskite-type systems with $\tau > 1$. In addition, the larger band gap of the material also restricts the current density. Cross sectional SEI of the devices [Figs. 4(b) and 4(c)] shows crystal growth of the 2D GA₂PbI₄ perovskite parallel to the TiO₂ substrate that limits electronic conductivity perpendicular to the Pb–I layers and reduces performance. As these materials exhibit temperature dependent morphism, device fabrication was carried out after annealing the GAPbI₃ films at 70 and 170 °C, with performance of the former much poorer ($\tau < 0.0002$, Table SI supplementary data), than for films annealed at 170 °C ($\eta = 0.16\%$). Two approaches for device fabrication to enhance J_{sc} were explored; (i) using a higher perovskite precursor concentration (1.2 M), and (ii) dispersing the perovskite powder in dimethyl formamide (DMF). However, these strategies did not lead to better performance (Table SII supplementary data). Thus obtained device efficiency is only 0.45% and further compositional engineering with mixed organic cations may be needed to enhance the device performance. During the preparation of the manuscript, the work was published by Yang et al., where they have reported, extraordinarily enhancement in the carrier lifetimes, higher device open circuit voltages and hence power conversion efficiency (exceeding 17%) in GA doped MAPbI₃ perovskites films than pure MAPbI₃ films.³⁰

2.4 Photoluminescence measurements

Figure 5 shows the PL spectra of GAPbI₃ (a) and GA₂PbI₄ (b) and, exhibiting a band edge emission that is overlapped with broad emission bands, which are possibly defect-related. In light of the weak PL from both materials, complementary transient absorption (TA) spectroscopy was performed to probe the

dynamics and study the carrier relaxation lifetimes [Figs. 5(c) and 5(d)]. The defect origins of this broad PL emission band are consistent with the observed weak absorption across the visible regime [see Figs. 5(c) and 5(d)]. Figure S7 supplementary data at shows the TA decay transients for the ground-state bleach (~ 483 nm for GA_2PbI_4 and ~ 474 nm for GAPbI_3) which were fitted using a tri-exponential decay function with the longest lifetime component lasting only <200 ps. The two shorter lifetimes (at few ps and tens of ps) are likely from the non-radiative trapping to the defect states. Such ultrafast trapping to defects=traps competes very effectively with charge extraction; consistent with the poor device efficiencies. Nonetheless, the origins of these traps warrant further investigations.

Fig. 5. (Color online) Fluence-dependent PL spectra of GAPbI_3 (a) and GA_2PbI_4 (b). TA spectra of GAPbI_3 (c) and GA_2PbI_4 (d) as a function of time. Excited at 400 nm with a pump fluence of $10 \mu\text{J cm}^{-2}$.

3 Conclusions

This work describes the photovoltaic properties of guanidinium (GA , CH_6N^{3+}) plumbate perovskite solar cells. GA_2PbI_4 was confirmed to be monoclinic ($P2_1/n$), with a $h00$ texture where the 2D perovskite Pb-I layers are parallel to the substrate surface. For GAPbI_3 , the crystal structure remains speculative, however a hexagonal perovskite containing chains of face sharing octahedra is proposed, analogous to the 1D hexagonal perovskites formed by materials with a tolerance factor $\tau > 1$. The optical band gaps for GAPbI_3 and GA_2PbI_4 are approximately the same, i.e., 2.48 and 2.52 eV and the device efficiencies are 0.16 and 0.45% respectively. Both samples are PL active at room temperature. TA spectroscopy strongly suggests that the PL is defect-related. Overall the device performance was poor compared to standard MAPbI_3 and FAPbI_3 perovskite systems. Nonetheless, this study provides guidance for designing guanidinium based perovskite absorbers for solar cell devices. In addition, through further compositional engineering with alternative or mixed organic cations it may be possible to enhance the device performance.

Acknowledgments

The financial support from a joint project initiative between Nanyang Technological University (NTU), Singapore and Johnson Matthey Centre U.K. is acknowledged. Author would like to thank Professor Subodh G. Mhaisalkar for his valuable suggestions and guidance for completion of this work. Author would like to thank Dr. Roman Kultyshev for his suggestion for GA cation and Dr. Fu Kunwu for assistance in device fabrication. The funding from National Research Foundation (NRF) Singapore through CRP

(NRF-CRP14- 2014-03) and SinBeRISE CREATE programme as well as support from NTU-A*STAR Silicon Technologies Centre of Excellence under the program grant No. 11235100003 and MOE Tier 1 grant RG184=14 is acknowledged. T.C.S. acknowledges the financial support from Nanyang Technological University start-up grant M4080514 and the Ministry of Education AcRF Tier 1 grant RG101=15 and Tier 2 grants MOE2013-T2-1-081 and MOE2014-T2-1-044.

- 1) M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science* **338**, 643 (2012).
- 2) G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, and T. C. Sum, *Nat. Mater.* **13**, 476 (2014).
- 3) S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, and S. G. Mhaisalkar, *Adv. Mater.* **28**, 6804 (2016).
- 4) A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, *J. Am. Chem. Soc.* **131**, 6050 (2009).
- 5) W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo, and S. I. Seok, *Science* **348**, 1234 (2015).
- 6) D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, and A. Hagfeldt, *Sci. Adv.* **2**, e1501170 (2016).
- 7) N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, and S. I. Seok, *Nature* **517**, 476 (2015).
- 8) N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. I. Seok, *Nat. Mater.* **13**, 897 (2014).
- 9) G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, and T. C. Sum, *Science* **342**, 344 (2013).
- 10) 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 (2016).
- 11) B. Wu, K. Fu, N. Yantara, G. Xing, S. Sun, T. C. Sum, and N. Mathews, *Adv. Energy Mater.* **5**, 1500829 (2015).
- 12) S. A. Kulkarni, T. Baikie, P. P. Boix, N. Yantara, N. Mathews, and S. Mhaisalkar, *J. Mater. Chem. A* **2**, 9221 (2014).
- 13) T. M. Koh, K. Fu, Y. Fang, S. Chen, T. C. Sum, N. Mathews, S. G. Mhaisalkar, P. P. Boix, and T. Baikie, *J. Phys. Chem. C* **118**, 16458 (2014).
- 14) N. Pellet, P. Gao, G. Gregori, T.-Y. Yang, M. K. Nazeeruddin, J. Maier, and M. Grätzel, *Angew. Chem., Int. Ed.* **53**, 3151 (2014).
- 15) H. Zhou, Q. Chen, G. Li, S. Luo, T. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang, *Science* **345**, 542 (2014).
- 16) 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* **3**, 23829 (2015).
- 17) J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H. Kim, A. Sarkar, Md. K. Nazeeruddin, M. Grätzel, and S. I. Seok, *Nat. Photonics* **7**, 486 (2013).
- 18) M. H. Kumar, S. Dharani, W. L. Leong, P. P. Boix, R. R. Prabhakar, T. Baikie, C. Shi, H. Ding, R. Ramesh, M. Asta, M. Grätzel, S. G. Mhaisalkar, and N. Mathews, *Adv. Mater.* **26**, 7122 (2014).
- 19) G. Giorgi, J.-I. Fujisawa, H. Segawa, and K. Yamashita, *J. Phys. Chem. C* **119**, 4694 (2015).
- 20) A. Katrusiak and M. Szafranski, *Acta Crystallogr., Sect. C* **50**, 1161 (1994).
- 21) W. Li, A. Thirumurugan, P. T. Barton, Z. Lin, S. Henke, H. H. M. Yeung, M. T. Wharmby, E. G. Bithell, C. J. Howard, and A. K. Cheetham, *J. Am. Chem. Soc.* **136**, 7801 (2014).
- 22) G. Kieslich, S. Sun, and A. K. Cheetham, *Chem. Sci.* **5**, 4712 (2014).
- 23) M. Szafranski, *Thermochim. Acta* **307**, 177 (1997).
- 24) L. Dimesso, A. Quintilla, Y. M. Kim, U. Lemmer, and W. Jaegermann, *Mater. Sci. Eng. B* **204**, 27 (2016).
- 25) M. Szafranski and A. Katrusiak, *Phys. Rev. B* **61**, 1026 (2000).
- 26) J. B. Goodenough and J. A. Kafalas, *J. Solid State Chem.* **6**, 493 (1973).
- 27) C. C. Stoumpos, C. D. Malliakas, and M. G. Kanatzidis, *Inorg. Chem.* **52**, 9019 (2013).
- 28) T. Chen, B. J. Foley, C. Park, C. M. Brown, L. W. Harriger, J. Lee, J. Ruff, M. Yoon, J. J. Choi, and S.-H. Lee, *Sci. Adv.* **2**, e1601650 (2016).
- 29) A. D. Jodlowski, A. Yépez, R. Luque, L. Camacho, and G. de Miguel, *Angew. Chem., Int. Ed.* **55**, 14972 (2016).
- 30) N. D. Marco, H. Zhou, Q. Chen, P. Sun, Z. Liu, L. Meng, E.-P. Yao, Y. Liu, A. Schiffer, and Y. Yang, *Nano Lett.* **16**, 1009 (2016).