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Mitzi, David B.

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Keith Hurka-Owen
Duke University
2200 W Main St STE 710
Durham, NC 27708-4677

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Lynne M Franciosi
Office of Naval Research
100 Alabama Street SW Suite 4R15
Atlanta, GA 30303-3104

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Melt Processing of Operationally-Stable Perovskite Photovoltaic Films and Devices

Grant Number: N000141712207

Reporting Period: 02/01/2017 – 10/31/2020 (Final Report)

Submitter: David Mitzi

Submitter Institution: Duke University

Abstract: Flexible, light weight, durable and high-performance photovoltaic (PV) systems based on organic-inorganic perovskite (OIP) semiconductors are expected to provide critical opportunities for combat operations, where mobile and off-grid power can vastly improve battlefield effectiveness. However, air, humidity and thermal sensitivity, as well as degradation under illumination, all contribute to questionable reliability for current generation devices. While deeper scientific underpinnings for OIP stability are forming, important empirical factors promoting stability include: 1) large grain size within the OIP layer to reduce access of air/moisture to the film interior; 2) more two-(as opposed to three-) dimensional perovskite crystal lattices in order to enable incorporation of less volatile and more hydrophobic (i.e., effective for repelling moisture) cations within the framework; 3) control over interfacial reaction and decomposition pathways at the OIP absorber/electron (or hole) transport layer interfaces; and 4) effective encapsulation to provide a "first line of defense" against prospective detrimental environmental agents such as moisture, air and UV light. This program has focused on demonstrating a novel film deposition approach—melt-processing—for Pb-based OIPs, which offers the prospects of addressing the above stability-promoting factors for PV absorber layers and providing a pathway for versatile high-throughput fabrication of potentially flexible PV devices.

Project Goals: Lead-halide-based hybrid organic-inorganic perovskite (HOIP) materials have been successfully integrated into photovoltaic (PV) devices as the absorber layer, yielding excellent power conversion efficiencies of >20%. However, device stability remains a major problem limiting their advance towards commercialization. This project aims to demonstrate that, using the melt processing approach as the film deposition method, it is possible to address several issues that influence the perovskite stability: 1) improving grain size to combat oxygen/moisture diffusion; 2) incorporating more stable 2D layered perovskites with preferred crystallographic orientation; 3) demonstrating more flexible choice of electron transport layer (ETL)/hole transport layer (HTL) materials (i.e., chosen freely, without concern for their deposition approach, even involving high temperatures and/or polar solvents) with benign interfacial properties and 4) effective device encapsulation/lamination for absorber layer protection.

Specific tasks include: 1. Designing and synthesizing lead halide-based perovskite compounds that have a melting transition before decomposition. The perovskites are selected from among the Ruddlesden-Popper family of general chemical formula $A'_2A_{n-1}Pb_nI_{3n+1}$, where A' is a large organic cation, A is a small organic cation, and n is a parameter that specifies the relative proportion of small to large organic cations and the dimensionality of the resulting crystal structure (lower n is associated with a lower proportion of small organic cations and a more 2D crystal structure, while higher n is associated with a higher proportion of small organic cations and a more 3D crystal structure); 2. Selecting and demonstrating target compounds with lower band gap energies as melt-processing candidates; 3. Developing melt-processing procedures and demonstrating perovskite film formation with good crystallinity and crystallographic orientation control, based on target compound structure and melt-processing conditions, such as a temperature gradient; 4. Exploring ETL and HTL options (mainly inorganic compounds) that are compatible with the perovskite layer and stable under melt-processing conditions (i.e., high temperature treatment); 5. Integrating all above-mentioned components into a laminated device structure using a one-step melt-processing approach and showing good device efficiency with improved stability and novel functionality.

Summary of Selected Accomplishments Under Goals:

- *Melt-processing of lead-iodide-based n=1 2D perovskites*: Using phenethylammonium (PEA) derivatives as the organic cation, n=1 layered lead iodide perovskites were studied as a model system. Results from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (***Fig. 1***) indicate that the Pb-based compounds decompose above 200 °C, while the melting temperature, T_m, is also typically above 200 °C. Like the Sn analogues, T_m values of Pb-based layered perovskites heavily depend on the organic cation structure (***Table 1***); substitutions near the N atom will lower T_m, while substitutions on the phenyl ring moving from the 2- to the 4- position will increase T_m. With a suitable choice of organic cation (β-Me-PEA), highly crystalline Pb-halide-based HOIP films were melt processed in air at moderate temperature (***Fig. 2a***). SEM images of melt-processed films show good coverage free of pinholes, with very large lateral grain size of at least 10 μm (***Fig. 2b***). The film thickness can be further tuned by the amount of sample loading and applied pressure during melting. The absorption and photoluminescence spectra of the melt-processed and spin-coated films also show no obvious difference (***Fig. 2c,d***). In summary, melt processed films of 2D Pb-based HOIPs, prepared in the ambient air and with high phase purity and crystallinity, have been demonstrated for the first time; thermal properties of 2D HOIPs are shown to be controllable using the organic cation. Results were published (*Chem. Mater.* 2017, 29, 6200).

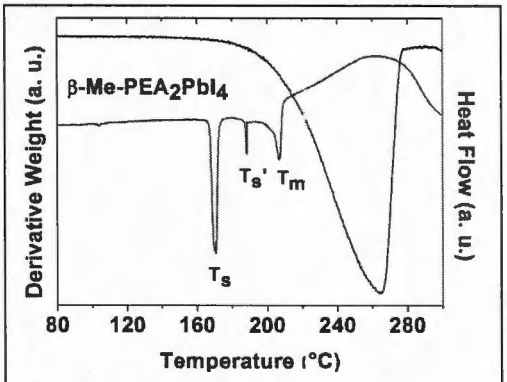


Fig. 1. TGA and DSC of $(\beta\text{-Me-PEA})_2PbI_4$ (from *Chem. Mater.* 2017, 29, 6200)

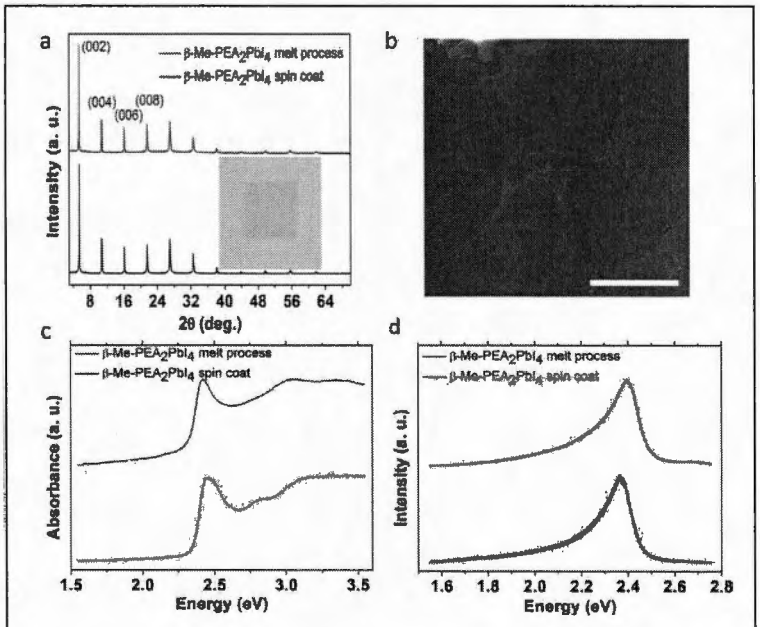
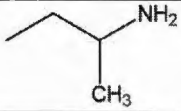
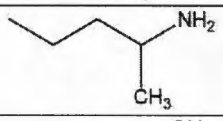
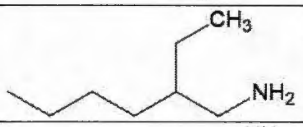
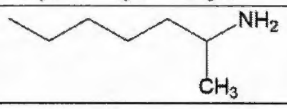


Fig. 2. (a) XRD patterns (square root scale) of spin-coated and melt-processed $(\beta\text{-Me-PEA})_2PbI_4$ films. (b) SEM image of melt-processed $(\beta\text{-Me-PEA})_2PbI_4$ films (scale bar 50 μm). Absorption (c) and PL (d) spectra of spin-coated and melt-processed $(\beta\text{-Me-PEA})_2PbI_4$ films. (from *Chem. Mater.* 2017, 29, 6200)

Table 1. Melting temperatures (T_m) of Sn- and Pb-iodide n=1 2D perovskites

	Sn	Pb
Organic cation	Melting T_m (°C)	Melting T_m (°C)
β-Me-PEA	170.0	207.0
2-F-PEA	200.8	245.8
4-MeO-PEA	210.1	247.1
PEA	213.4	252.9
3-F-PEA	233.0	261.4
4-F-PEA	234.2	258.9

Table 2. Transition temperatures of 2D Pb-I perovskites extracted from DSC

Organic cation	Cation structure	Structural transition (°C)	Melting transition T_m (°C)
n-ba		-	296.9
n-ha		82.5/102.0	290.1
1-Me-pa		-	235.0
1-Me-ba		115.2	195.3
2-Et-ha		118.7/174.6	178.2
1-Me-ha		111.1/167.8	172.3

- *Melting temperature suppression via organic cation branching*: To further investigate whether proposed design rules for low T_m apply to a wider range of organic cations and to create hybrid candidates that melt at much lower temperature than decomposition, we extended our effort into alkylammonium-based lead iodide perovskites. Six perovskite compounds with different alkylammonium chain length and structure were synthesized. We found that, by modifying the alkylammonium cation structure—e.g., extending the alkyl chain length and introducing branching (side chains)—it is possible to create target compounds with T_m of as low as ~170 °C, well below the decomposition temperature (***Table 2***). As observed in the previous PEA-based systems, substitutions (branching or side chains) on the alkyl chain near the ammonium group significantly lower T_m (by >100 °C). Secondly, for organic cations with a similar structure (i. e. side chain at the same position), a longer alkyl chain leads to lower T_m. These findings, along with results for PEA-based systems, indicate that introducing substitution (branching) near the ammonium group is a general method to lower the melting temperature of 2D HOIPs. Additionally, the new hybrids were structurally determined by single crystal

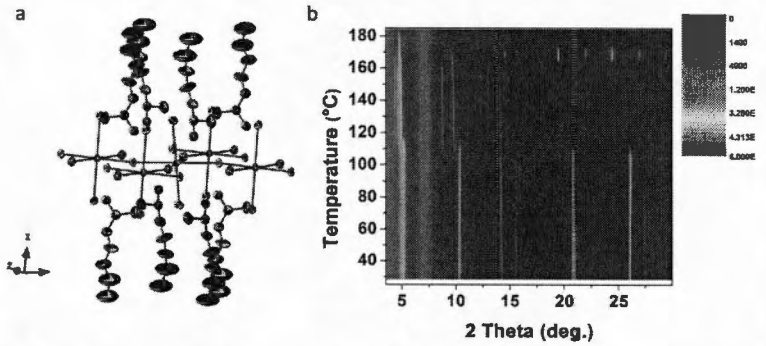


Fig. 3. (a) crystal structure of $(1\text{-Me-ha})_2PbI_4$ and (b) *in-situ* temperature-dependent XRD pattern of $(1\text{-Me-ha})_2PbI_4$ between 30 °C and 180 °C. (from *Chem. Sci.* 2019, 10, 1168)

XRD (***Fig. 3a***). The solid-to-melting process was monitored by in-situ temperature-dependent XRD (***Fig. 3b***). Overall, the approach of suppression of T_m via alkyl chain branching provides a comfortable temperature window for solvent-free melt-processing of lead iodide HOIP films with minimal energy input. These findings can be formulated into design rules to guide the discovery of other new low T_m HOIPs. Published as (*Chem. Sci.* 2019, 10, 1168).

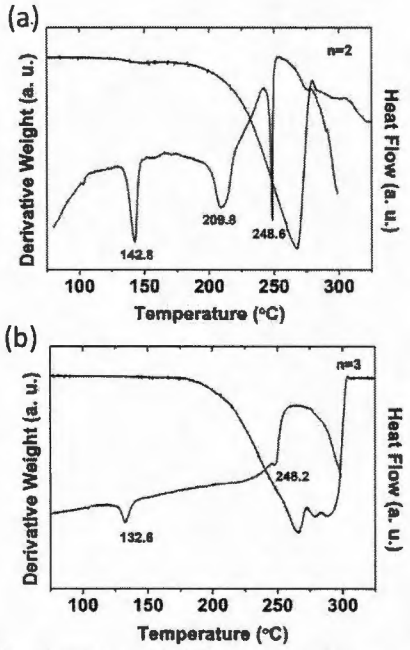


Fig. 4. TGA and DSC curves of (a) n=2 and (b) n=3 β-Me-PEA based compounds. (*Chem. Sci.* 2019, 10, 1168)

- *Melt processing of n>1 layered lead iodide perovskites*: β-Me-PEA-based higher n compounds with smaller band gap—i.e., compounds with n=2 and 3: $(\beta\text{-Me-PEA})_2MAPb_2I_7$ and $(\beta\text{-Me-PEA})_2MA_2Pb_3I_{10}$)—were synthesized and examined for melting transitions. The TGA/DSC curves (***Fig, 4a,b***) show that these higher-n compounds are stable up to 200 °C, similar to the n=1 compound. Multiple structural transitions are observed from DSC scans and, compared to the n=1 compound, the melting transition temperatures move up considerably to 248.6 °C and 248.2 °C, respectively, for n=2 and 3. T_m values of these phases are all above the decomposition temperature and the compounds do not melt congruently. However, through the introduction of a post-annealing step at 150 °C after partial melting, and with careful tuning of the amount of the organic ammonium salt additives, ambient air melt-processing of these higher-n phases can be achieved and *highly crystalline* and *phase-pure* films can be made (***Fig. 5 a-c***), contrary to what is commonly observed in spin-coated

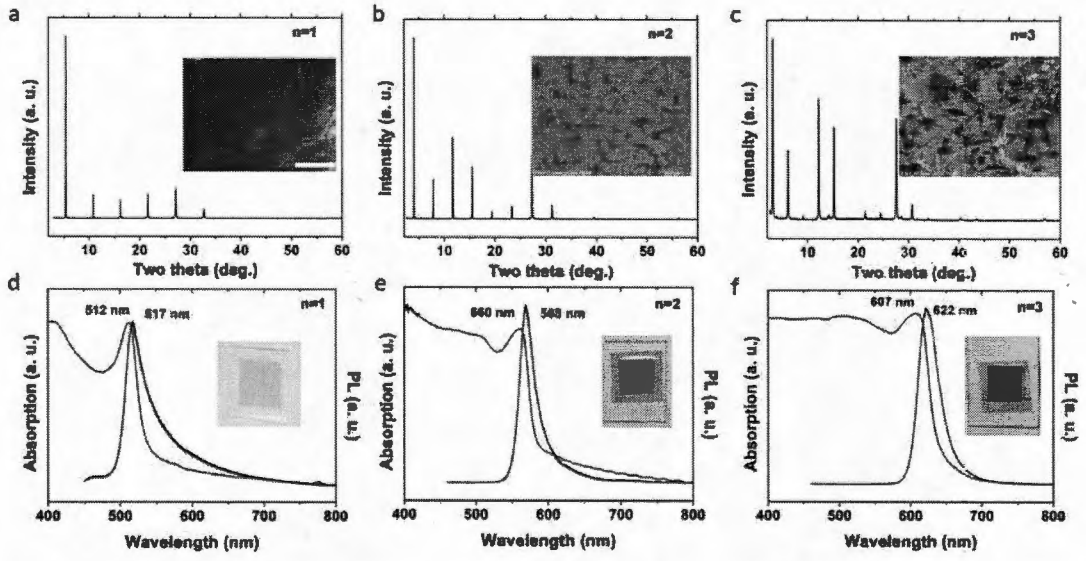


Fig. 5. XRD, SEM images (inset), absorption and PL spectra of n=1 (a, d), n=2 (b, e) and n=3(c, f) phases. (from *Chem. Mater.* 2019, 31, 4267)

analogs. It is worth noting that all films show strong preferred orientation, with inorganic layers lying parallel to the substrate, as evident from the (00l) peaks in the XRD patterns. The work was published (*Chem. Mater.* 2019, 31, 4267).

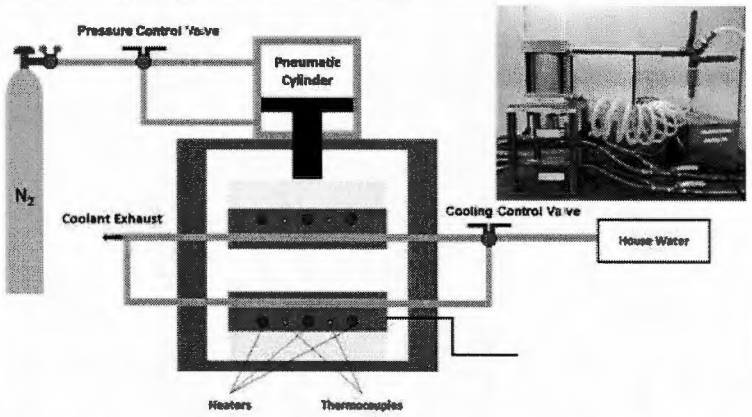


Fig. 6. Schematic (and inset picture of finished tool) of the custom-built hot press with pressure control and rapid cooling features.

- *Designed/fabricated a melt-processing tool for HOIP semiconductors*: To subject perovskite films to processing conditions that are suitable for melting and laminating, we constructed a custom-designed hot press (***Fig. 6***), with independently temperature-controlled top and bottom plates (with water coolant for rapid cooling) and pneumatic pressure control.

- *Perovskite interfacial stability with HTL/ETL under lamination conditions*: It is often considered that perovskite ($MAPbI_3$) and the inorganic electron-/hole-transport layer (ETL/HTL) materials like SnO_2 and NiO_x form chemically stable interfaces at temperatures of up to 100 °C. For hot-pressing and lamination processes, the target temperature is typically above this point. Therefore, we studied the behavior of $MAPbI_3$ films as well as NiO_x/SnO_2 layers under lamination conditions. When confined under pressure, $MAPbI_3$ is surprisingly stable up to 200 °C with minimal decomposition detected by XRD. Significant grain growth is observed when annealed above 150 °C (***Fig. 7***). Efficiency of devices made under lamination conditions remains relatively stable with increasing temperature when SnO_2 is used as ETL, while it decreases drastically when NiO_x is used as HTL (***Fig. 8***). This indicates that NiO_x is not compatible with the perovskite layer at high temperatures, while SnO_2 may be useful for lamination processing. The interfacial stability of NiO_x was then further investigated by testing the reactivity with MAI and $MAPbI_3$; NiO_x is found to readily react with MAI (a component of $MAPbI_3$) when annealed above 100°C, forming NiI_2. When used as the HTL in solar cell devices, the $NiO_x/MAPbI_3$ interface is therefore not inert. Similar study on SnO_2 with MAI and $MAPbI_3$ also results in the formation of

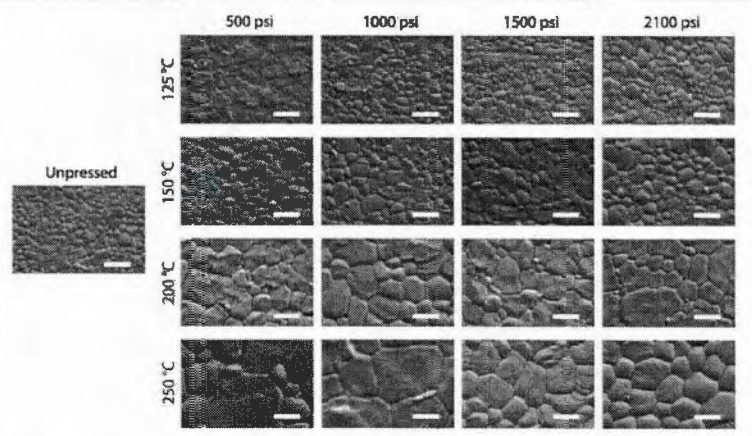


Fig. 7. Top-view SEM images of $MAPbI_3$ films on glass, hot pressed for 1 minute at the specified temperature and pressure (all scale bars 1 μm) (from *ACS Appl. Energy Mater.* 2019, 2, 5083).

SnI_4, but the degree of such reaction is significantly lower. These observations account for the drop in NiO_x-based device efficiencies when treated under lamination conditions and more generally highlight the importance of considering interfacial reactivity when pursuing laminated devices. This work was published (*ACS Appl. Energy Mater.* 2019, 2, 5083).

- *Comprehensive review on "Synthetic Approaches for Halide Perovskite Thin Films" published*: PI Mitzi and PhD student Wiley Dunlap-Shohl published a comprehensive review in *Chemical Reviews*, which details (article is >100 pages) the many different halide perovskite film deposition approaches (including melt processing), along with underlying physical principals governing the deposition. It is expected that this article (*Chem. Rev.* 119, 3193, 2019) will become a "go to" reference for researchers in the field (especially new researchers). The review is already cited 180 times (Google Scholar accessed on March 16, 2021).

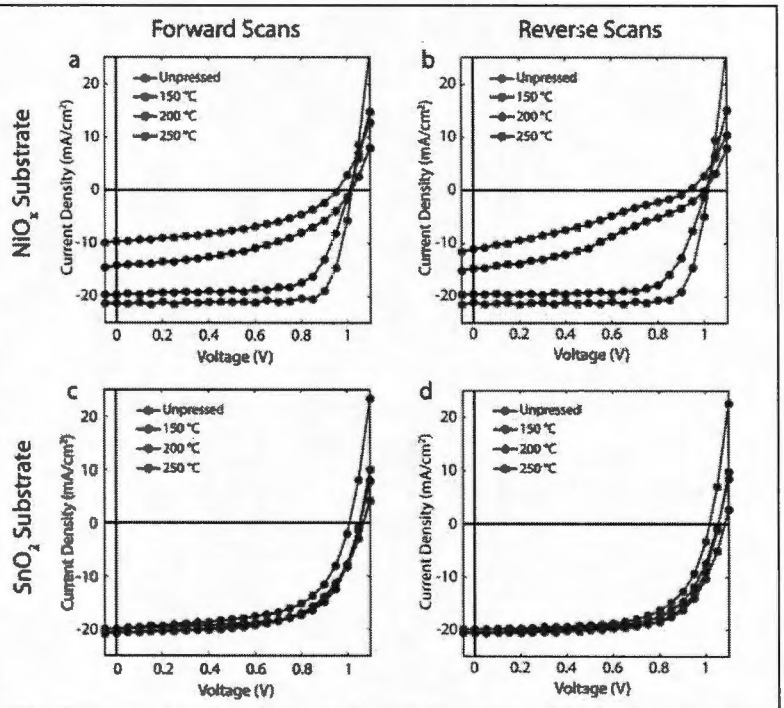


Fig. 8. Forward (a,c) and reverse (b,d) J–V sweeps of the best-performing hot-pressed (at 500 psi film pressure) $MAPbI_3$ solar cells using an ITO/NiO_x/$MAPbI_3$/C_{60}/BCP/Ag (a,b) or ITO/SnO_2/$MAPbI_3$/Spiro-OMeTAD/Au (c,d) architecture (*ACS Appl. Energy Mater.* 2019, 2, 5083).

- *Bifacial laminated device using $MAPbI_3$ as absorber*: Although both SnO_2 and NiO_x may react with $MAPbI_3$ or its precursors under lamination temperatures, devices based on the former are considerably more stable than the latter. Therefore, SnO_2 is used as the basis for laminated device construction. To bond the device halves together, we employ a method using a conductive meltable glue consisting of D-sorbitol and PEDOT:PSS as the adhesive. Pressing the half-devices together at 120 °C allows the D-sorbitol to melt; when cooled, it resolidifies, bonding the substrates together. The completed device architecture is ITO/SnO_2/PCBM/$MAPbI_3$/Spiro-OMeTAD/D-sorbitol/PEDOT:PSS/ITO. 4-tBP and Li-TFSI dopants are not included in the Spiro-OMeTAD HTL, due to concerns that they might diffuse into other device layers during lamination. The absence of dopant in these initial devices may contribute to a higher series resistance. Devices laminated at the above temperature for 1 min at ~2800 psi film pressure appear well-bonded across most of the electrodes (***Fig. 9***). The average J_{sc} is 19.13 mA/cm^2, while the V_{oc}, fill factor, and power conversion efficiency as measured from forward (reverse) I–V sweeps are 1.014 V (1.009 V), 50.3 % (56.1 %), and 9.8 % (10.8 %). The champion device reaches a forward (reverse) sweep efficiency of 11.8% (12.6%), with minimal hysteresis (***Fig. 9***). The EQE spectrum of this device reaches a maximum of ~90%, unambiguous proof that the device is highly efficient at absorbing

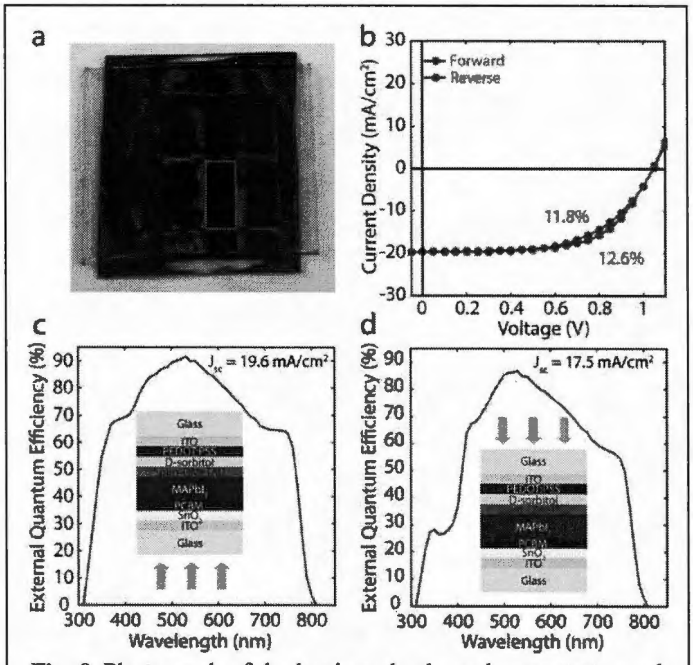


Fig. 9. Photograph of the laminated sub- and superstrate stack containing the champion device (at time of publication), indicated by the red rectangle (a); *J–V* curves of this device, collected using a 1 s measurement delay (b); EQE spectra of this device when illuminated through the ETL (c) or HTL side (d). (from *ACS Appl. Energy Mater.* 2, 5083, 2019)

and extracting carriers. A potentially useful feature of these PV devices is that they are bifacial, allowing light to be collected from either the front or the back side. Comparison of the EQE spectra of the champion device when illuminated from the ETL versus the HTL side shows that the former configuration is ~15% more efficient overall (J_{sc} = 19.6 mA/cm^2) than the latter (J_{sc} = 17.5 mA/cm^2), but that both are reasonably effective. The above results are reported in a publication (*ACS Appl. Energy Mater.* 2, 5083, 2019). The devices were further optimized (thickness of $MAPbI_3$ and HTL layers, HTL additive incorporation, and processing improvements) and the bifacial nature of these devices explored (*ACS Appl. Energy Mater.* 3, 9493, 2020), providing ultimately PCEs of 15+% and potential for up to 30% performance enhancement above this value due to albedo light and the bifacial nature.

- *Demonstration of a reversible glass-crystalline transition in a hybrid perovskite*: While most low-T_m hybrid perovskites developed under this project rapidly crystallize when cooled from the melt, we discovered that a bulky chiral organic cation effectively suppresses crystallization such that, if the melt is cooled at a rate >20 °C/min, a glass phase can readily be accessed (demonstrated for the first time in a HOIP at ambient pressures). The glass transition and crystallization temperatures were characterized, and we were able to show reversible switching between a glassy and crystalline state, each with distinct optical properties (***Fig. 10***). Such a material may be useful for low-power (low-temperature) phase change applications (e.g., energy storage, phase change memory, reconfigurable optics). The work was published (*Adv. Mater.* 33, 202005868, 2021) and a related provisional patent application was submitted.

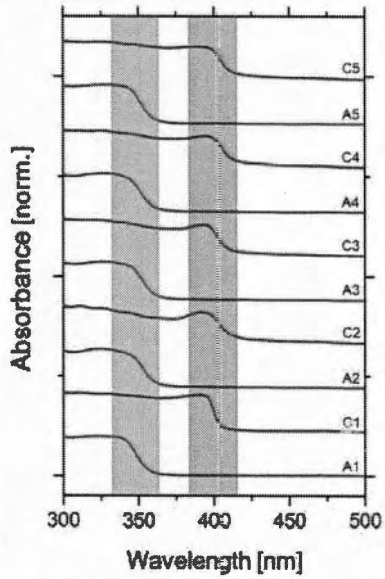


Fig. 10. UV-Visible absorbance spectroscopy of [S-(−)-1-(1-naphthyl)-ethylammonium]$_2PbBr_4$ over several thermal cycles showing reversible switching over 5 iterations. (from *Adv. Mater.* 33, 202005868, 2021)

Results Dissemination:

The primary mode of dissemination has involved publication of results in peer-reviewed journals, with currently 8 papers appearing in final form, as listed below:

- T. Li, W. A. Dunlap-Shohl, Q. Han, D. B. Mitzi, "Melt Processing of Hybrid Organic-Inorganic Lead Iodide Layered Perovskites," *Chem. Mater.* 29, 6200-6204, 2017.
- T. Li, W. A. Dunlap-Shohl, E. W. Reinheimer, P. Le Magueres, D. B. Mitzi, "Melting Temperature Suppression of Layered Hybrid Lead Iodide Perovskites via Organic Ammonium Cation Branching," *Chem. Sci.* 10, 1168-1175, 2019.
- W. A. Dunlap-Shohl, Y. Zhou, N. P. Padture, D. B. Mitzi, "Synthetic Approaches for Halide Perovskite Thin Films," *Chem. Rev.* 119, 3193-3295, 2019.
- T. Li, A. M. Zeidell, G. Findik, W. A. Dunlap-Shohl, J. Euvrard, K. Gundogdu, O. D. Jurchescu, D. B. Mitzi, "Phase-pure Hybrid Layered Lead Iodide Perovskite Films Based on A Two-Step Melt Processing Approach," *Chem. Mater.* 31, 4267-4274, 2019.
- W. A. Dunlap-Shohl, T. Li, D. B. Mitzi, "Interfacial Effects during Rapid Lamination within $MAPbI_3$ Thin Films and Solar Cells," *ACS Appl. Energy Mater.* **2**, 5083-5093, 2019.
- T. Li, W. A. Dunlap-Shohl, D. B. Mitzi, "Bifacial Perovskite Solar Cells via a Rapid Lamination Process," *ACS Appl. Energy Mater.* **3**, 9493-9497, 2020.
- F. Ye, H. Wu, M. Qin, S. Yang, G. Niu, X. Lu, J. Wang, D. B. Mitzi, W. C. H. Choy, "High-Quality $MAPbBr_3$ Cuboid Film with Promising Optoelectronic Properties Prepared by a Hot Methylamine Precursor Approach," *ACS Appl. Mater. Interfaces* **12**, 24498-24504, 2020
- Singh, M. K. Jana, D. B. Mitzi, "Reversible Crystal-Glass Transition in a Metal Halide Perovskite," *Adv. Mater.* **33**, 2005868, 2021.

Notably, graduate student Wiley Dunlap-Shohl and PI Mitzi spearheaded a major (over 100 pages) review on thin-film deposition (*Chem. Rev.* 2019, 119, 3193-3295), "Synthetic Approaches for Halide Perovskite Thin Films", which included discussion of melt processing for HOIP films. This article was part of a *Chemical Reviews* special issue on perovskites, for which PI Mitzi served as guest editor.

Another significant dissemination pathway involved numerous (>25) contributed, invited and keynote talks, seminars and poster presentations at Duke, other universities, conferences, and ONR program reviews.

Honors and Awards:

David Mitzi – Elected MATERIALS RESEARCH SOCIETY (MRS) FELLOW "For ground-breaking research in solution–processed inorganic and hybrid inorganic–organic semiconductors, and for their application for energy conversion and high-performance electronics" (2018)

David Mitzi – 2020 ACS AWARD IN THE CHEMISTRY OF MATERIALS, for "pioneering contributions to the discovery, fundamental chemistry, processing, and application of halide perovskite semiconductors, including the demonstration of high-performance hybrid organic-inorganic electronic devices".

David Mitzi – CLARIVATE ANALYTICS HIGHLY CITED RESEARCHER (top 1% by citation) for 2018, 2019, 2020.

David Mitzi – Served as GUEST EDITOR—Thematic issue on "Perovskites" for Chemical Reviews (ACS, impact factor of 52.6) – March 13, 2019 (Vol. 119, Issue 5)

Wiley Dunlap-Shohl – PhD student OUTSTANDING DISSERTATION AWARD (MEMS Department, Duke University, 2019)

Training Opportunities:

One postdoctoral (Dr. Tianyang Li) and two PhD (Wiley Dunlap-Shohl and Akash Singh) researchers performed the project work. They have all received training and experience on using new research tools (e.g., single crystal X-ray diffractometer, custom-designed melt-processing tool, thermal analysis, film deposition, solar cell fabrication and characterization), presenting results in group meetings/academic seminars/conferences, interacting and collaborating with internal and external researchers, and writing proposals for further funding applications. As an example of external connection, Tianyang Li interacted with Prof. Oana Jurchescu at Wake Forest University to incorporate melt processed films into thin-film transistor devices (as a way to access electronic properties of the melt-processed films) and collaborated with Prof. Kenan Gundogdu at NC State to study the photophysical properties of melt processed films. Dr. Li is now (as of April 2020) a staff member at Applied Materials in CA. Wiley Dunlap-Shohl successfully defended his PhD thesis (March 2019; containing work from this project—i.e., Chapter 4) and is now a postdoctoral researcher within Hugh Hillhouse's group at University of Washington. Akash Singh is a continuing PhD student within my group.

Technology Transfer: We submitted (May 2020) a provisional disclosure ("Organic-Inorganic Metal Halide Glass") describing a reversible glass-crystal transition in halide perovskite semiconductors, which could be impactful in phase-change memory and optical communication. This provisional will be upgraded to a regular disclosure prior to May 2021.

Participants: PI=Principal Investigator; PD=Postdoc; GS=Graduate Student

David Mitzi (PI)	1 Mo (yr 1); 1 Mo (yr 2); 1 Mo (yr 3+NCE)
Tianyang Li (PD)	12 Mo (yr 1); 8 Mo (yr 2); 10 Mo (yr 3+NCE)
Wiley Dunlap-Shohl (GS)	4 Mo (yr 2); 2 Mo (yr 3+NCE)
Akash Singh (GS)	7 Mo (Yr 3+NCE)