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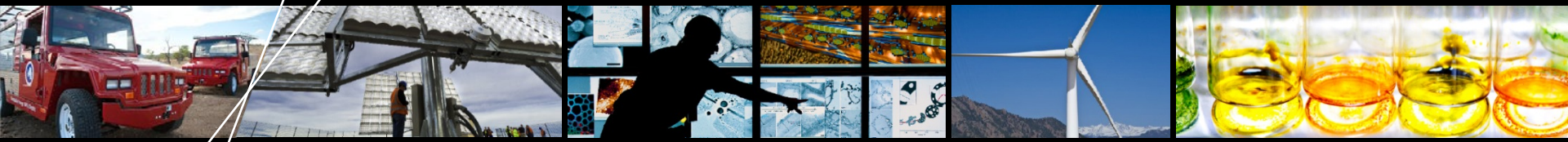

Perovskite PV (SUN UP)

SuNLaMP project 30291

Best Research-Cell Efficiencies

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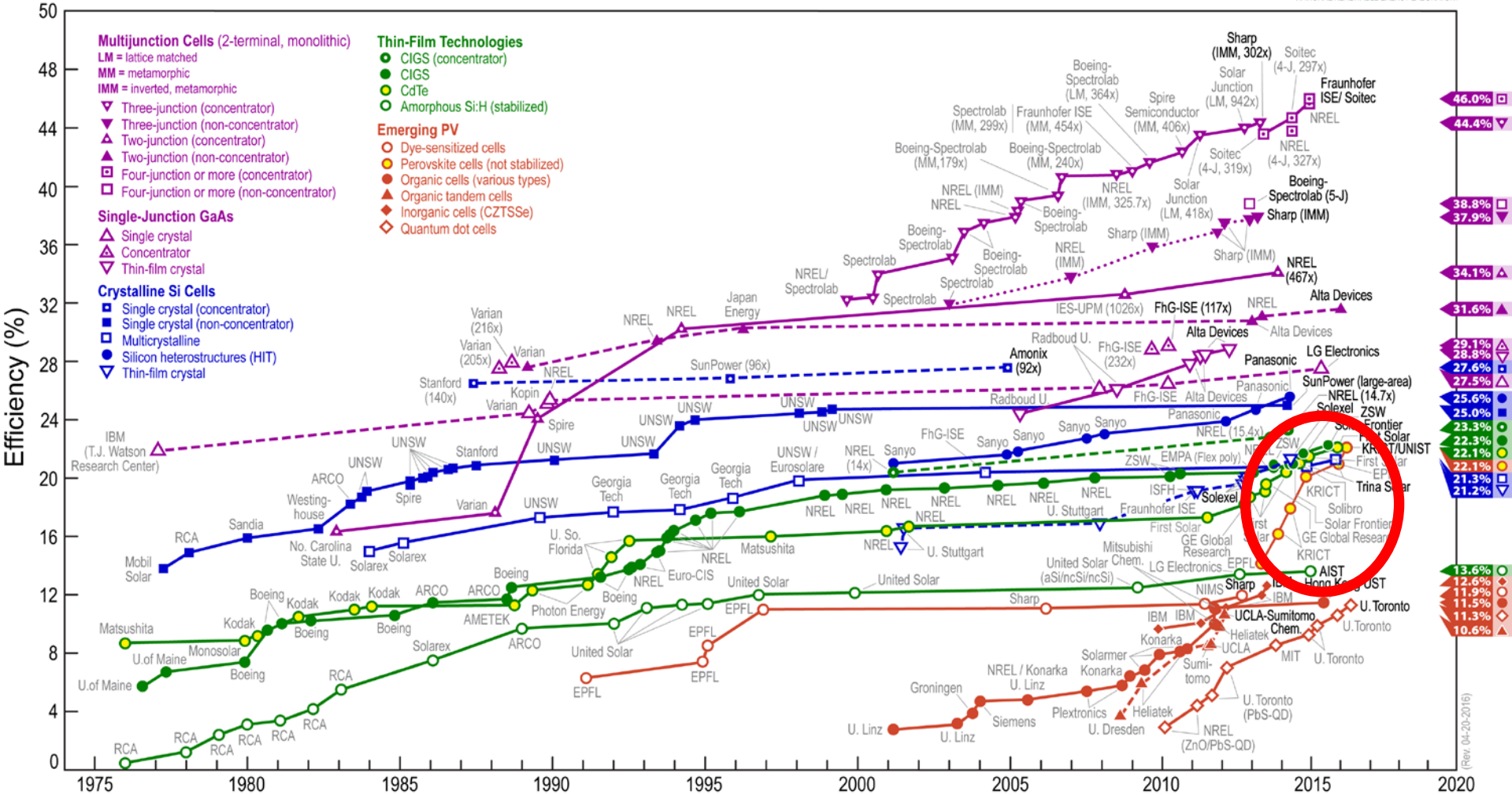
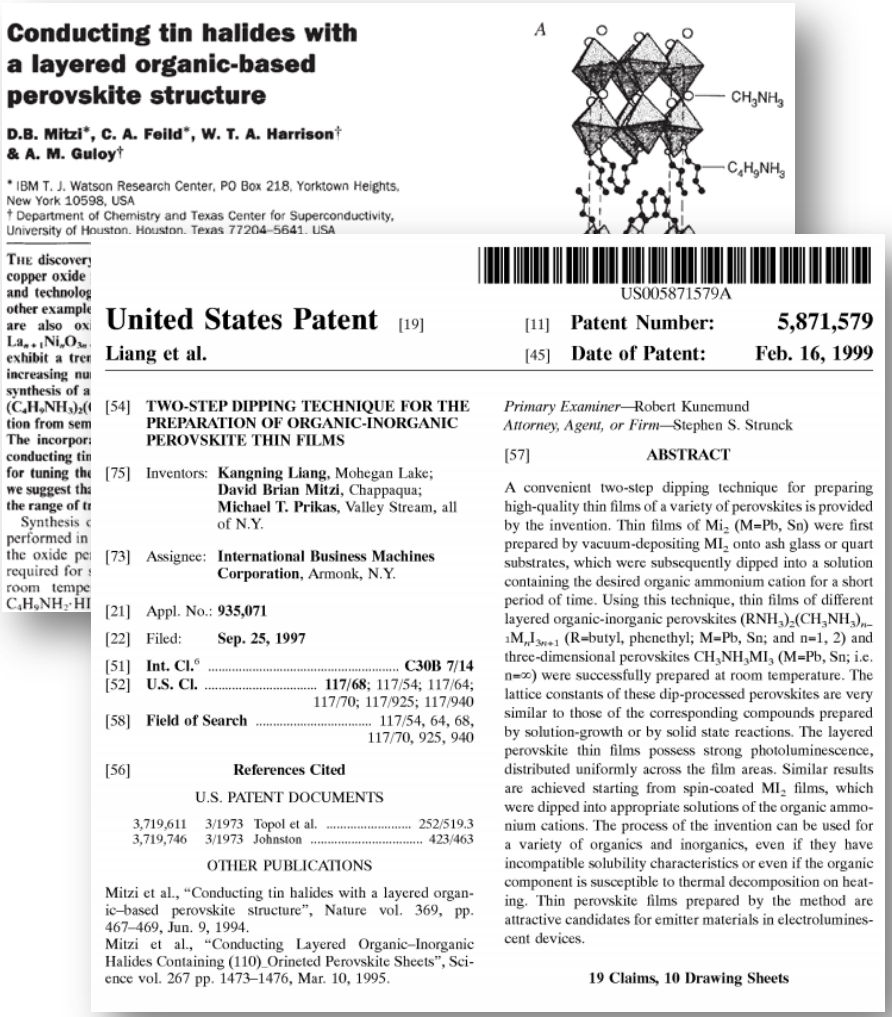


http://www.nrel.gov/ncpv/

Note on emerging PV: Lab scale, “un-stabilized” or other caveats

Before Perovskite PV and post 2009



Conducting tin halides with a layered organic-based perovskite structure

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A

CH_3NH_3

$C_4H_9NH_3$

THE discovery copper oxide and technolog other example are also ox $La_{n+1}Ni_nO_{3n}$ exhibit a tren increasing nu synthesis of a $(C_4H_9NH_3)_2($ tion from sem The incorpora conducting tin for tuning the we suggest tha the range of tr

Synthesis c performed in the oxide pe required for s room tempe $C_4H_9NH_2 \cdot HI$

US005871579A

United States Patent [19]

Liang et al.

[11] **Patent Number: 5,871,579**

[45] **Date of Patent: Feb. 16, 1999**

[54] **TWO-STEP DIPPING TECHNIQUE FOR THE PREPARATION OF ORGANIC-INORGANIC PEROVSKITE THIN FILMS**

[75] Inventors: **Kangning Liang**, Mohegan Lake; **David Brian Mitzi**, Chappaqua; **Michael T. Prikas**, Valley Stream, all of N.Y.

[73] Assignee: **International Business Machines Corporation**, Armonk, N.Y.

[21] Appl. No.: **935,071**

[22] Filed: **Sep. 25, 1997**

[51] **Int. Cl.**[6] **C30B 7/14**

[52] **U.S. Cl.** **117/68**; 117/54; 117/64; 117/70; 117/925; 117/940

[58] **Field of Search** 117/54, 64, 68, 117/70, 925, 940

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,719,611 3/1973 Topol et al. 252/519.3
3,719,746 3/1973 Johnston 423/463

OTHER PUBLICATIONS

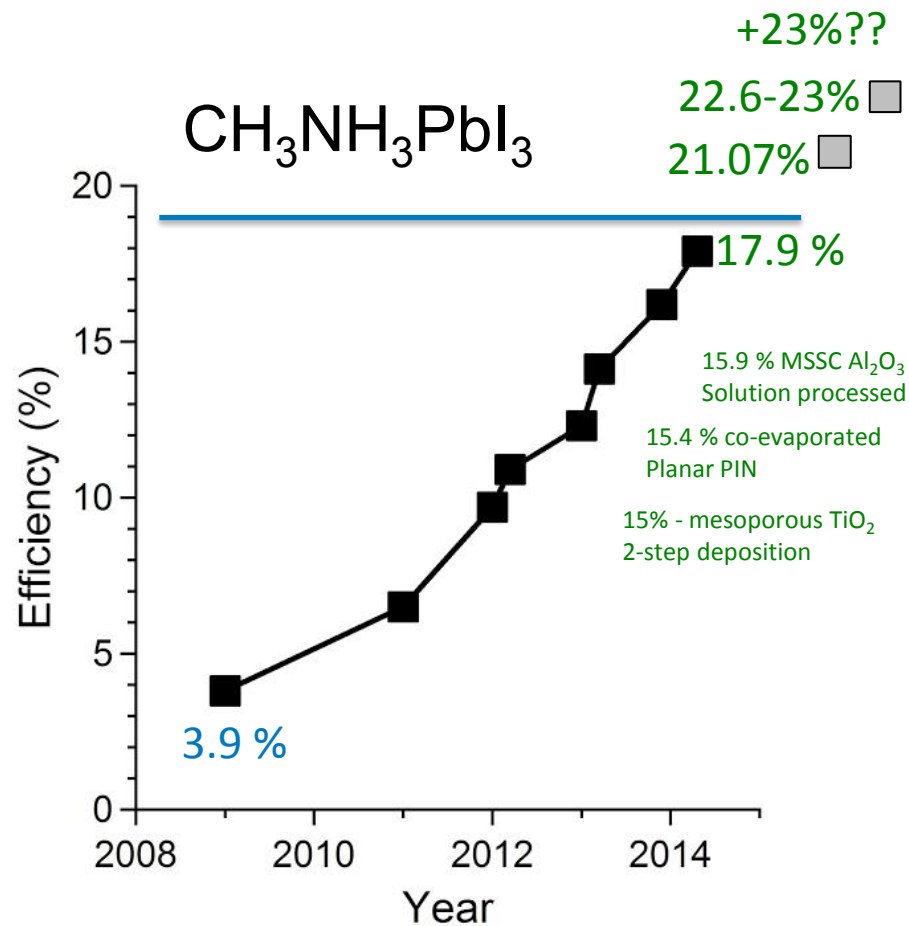
Mitzi et al., "Conducting tin halides with a layered organic–based perovskite structure", Nature vol. 369, pp. 467–469, Jun. 9, 1994.
Mitzi et al., "Conducting Layered Organic–Inorganic Halides Containing (110)_Orineted Perovskite Sheets", Science vol. 267 pp. 1473–1476, Mar. 10, 1995.

Primary Examiner—Robert Kunemund
Attorney, Agent, or Firm—Stephen S. Strunck

[57] **ABSTRACT**

A convenient two-step dipping technique for preparing high-quality thin films of a variety of perovskites is provided by the invention. Thin films of Mi_2 (M=Pb, Sn) were first prepared by vacuum-depositing MI_2 onto ash glass or quart substrates, which were subsequently dipped into a solution containing the desired organic ammonium cation for a short period of time. Using this technique, thin films of different layered organic-inorganic perovskites $(RNH_3)_2(CH_3NH_3)_{n-1}M_nI_{3n+1}$ (R=butyl, phenethyl; M=Pb, Sn; and n=1, 2) and three-dimensional perovskites $CH_3NH_3MI_3$ (M=Pb, Sn; i.e. n=∞) were successfully prepared at room temperature. The lattice constants of these dip-processed perovskites are very similar to those of the corresponding compounds prepared by solution-growth or by solid state reactions. The layered perovskite thin films possess strong photoluminescence, distributed uniformly across the film areas. Similar results are achieved starting from spin-coated MI_2 films, which were dipped into appropriate solutions of the organic ammonium cations. The process of the invention can be used for a variety of organics and inorganics, even if they have incompatible solubility characteristics or even if the organic component is susceptible to thermal decomposition on heating. Thin perovskite films prepared by the method are attractive candidates for emitter materials in electroluminescent devices.

19 Claims, 10 Drawing Sheets



Meteoric rise of efficiency in PV Performance

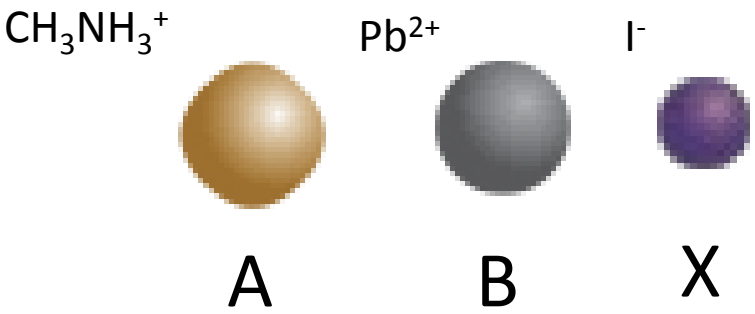
D. B. Mitzi, C. A. Feild, W. Harrison, and A. M. Guloy, "Conducting tin halides with a layered organic-based perovskite structure," *Nature*, vol. 369, r

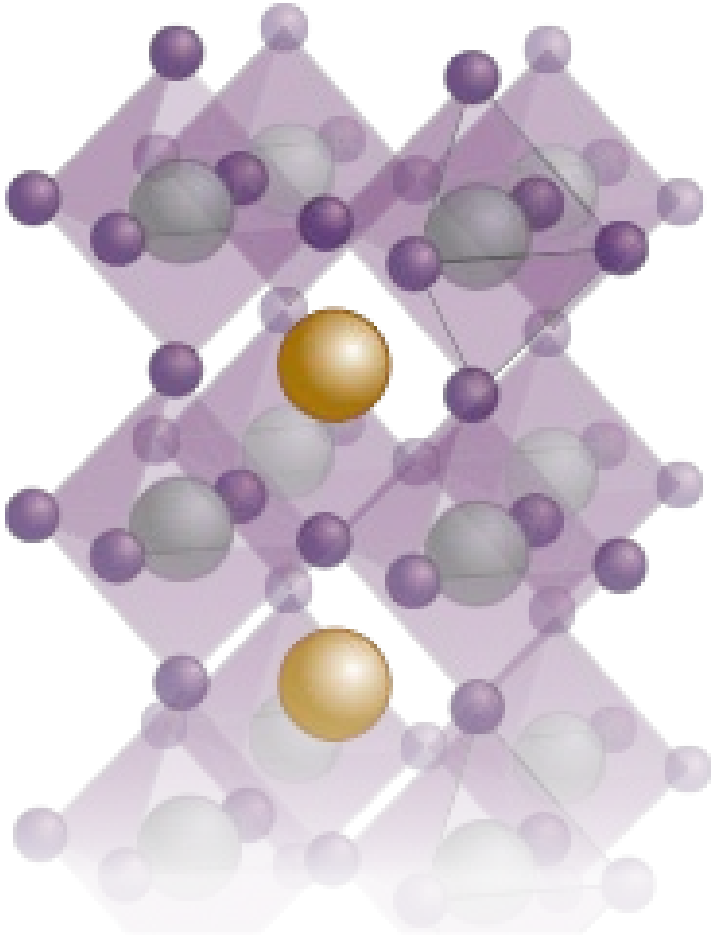
Solar 'Perovskite'

A = {*Methylammonium, Formamidinium, Cs …*}

B = {Pb, Sn, … }

X = {Br, I, … }





Generic formula: ABX_3

Notable work by Mitzi in transistors

B. Saparov and D. B. Mitzi, "Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design," *Chem. Rev.*, pp. acs.chemrev.5b00715–39, Apr. 2016.

Band gap tuning (solution processed GaAs)

Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells

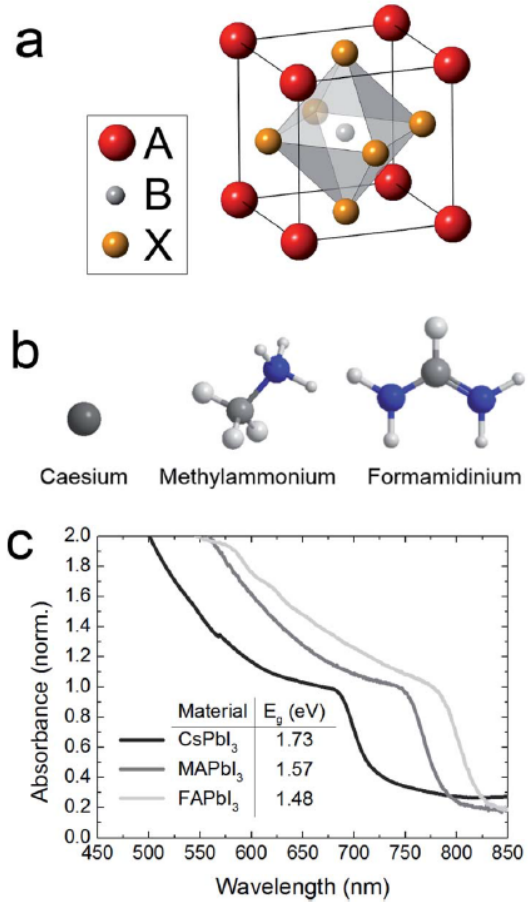


Fig. 1 Tuning perovskite bandgap by replacing the A cation. (a), The ABX_3 perovskite crystal structure. (b) The atomic structure of the three A site cations explored. (c) UV-Vis spectra for the $APbI_3$ perovskites formed, where A is either caesium (Cs), methylammonium (MA) or formamidinium (FA).

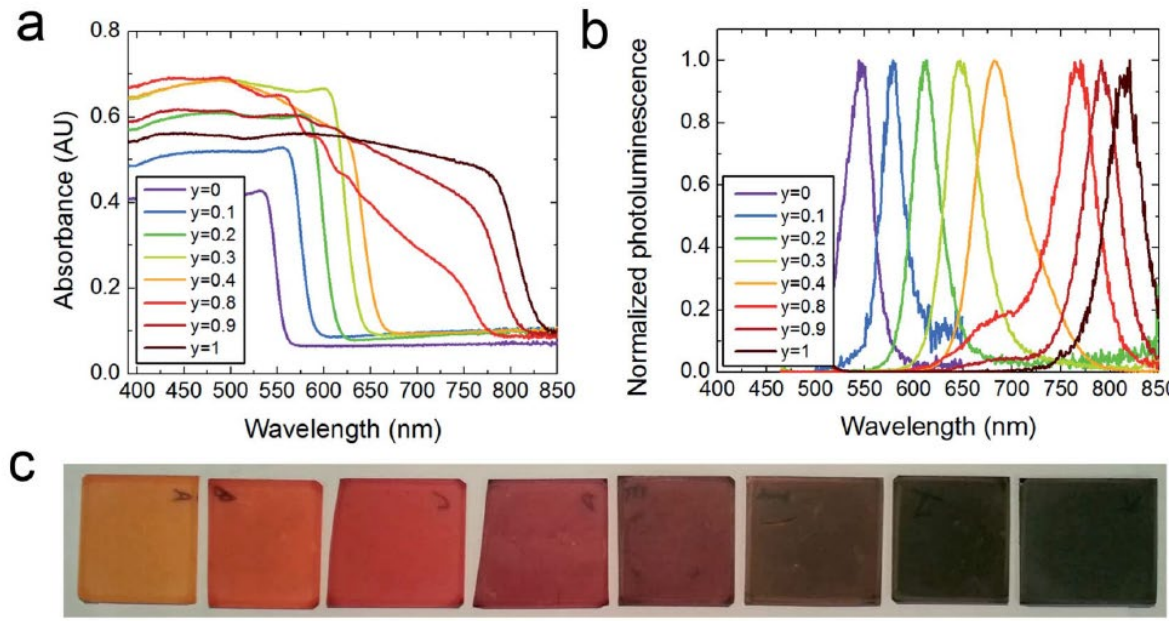


Fig. 2 Tunability of the $FAPbI_yBr_{3-y}$ perovskite system. (a) UV-Vis absorbance of the $FAPbI_yBr_{3-y}$ perovskites with varying y, measured in an integrating sphere. (b) Corresponding steady-state photoluminescence spectra for the same films. (c) Photographs of the $FAPbI_yBr_{3-y}$ perovskite films with y increasing from 0 to 1 (left to right). (d) XRD spectra of $FAPbI_yBr_{3-y}$ films showing the shift of the 100 (cubic) perovskite peak to the

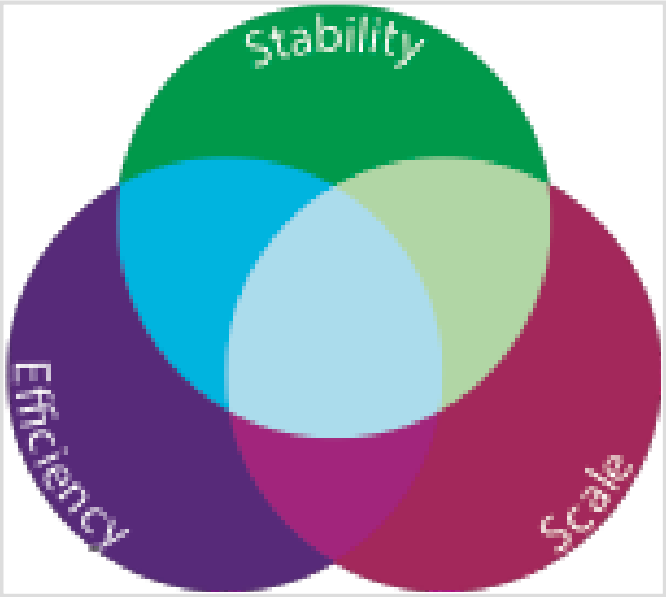
Relative sizes of all components determine strain and optoelectronic properties

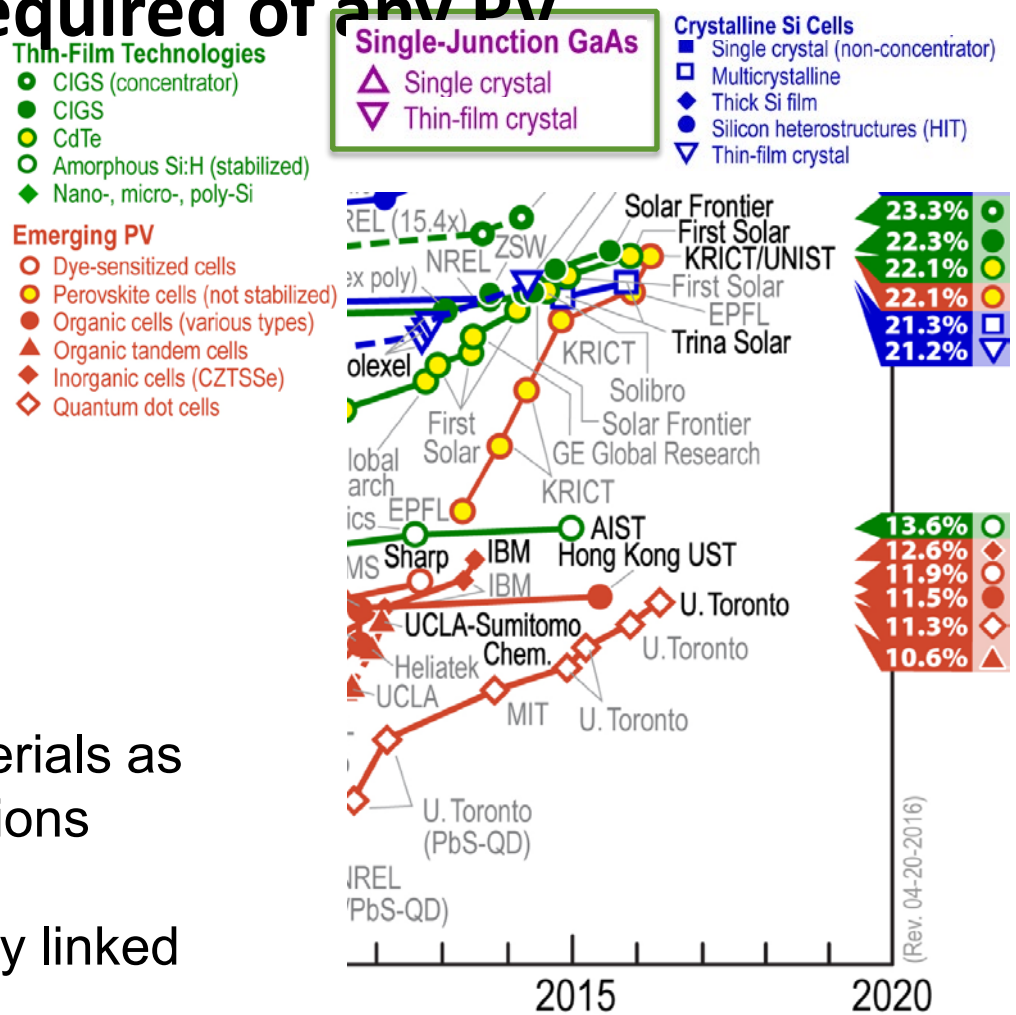
Eperon et al. *Energy Environ. Sci.*, **7**, 982 (2014)

Eperon, Snaith et al. Adv Funct. Mat. 2014

Requirements

- **Three critical elements required of any PV**



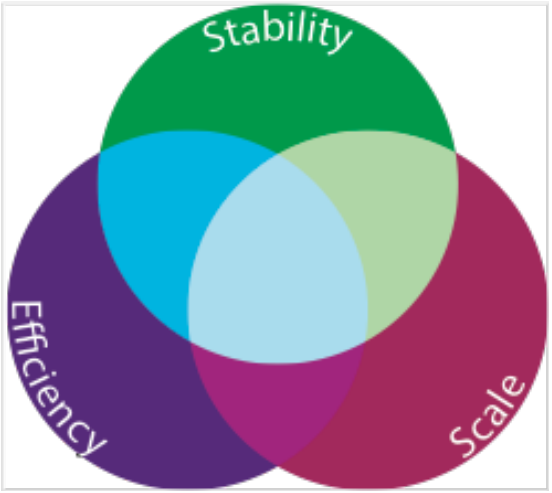


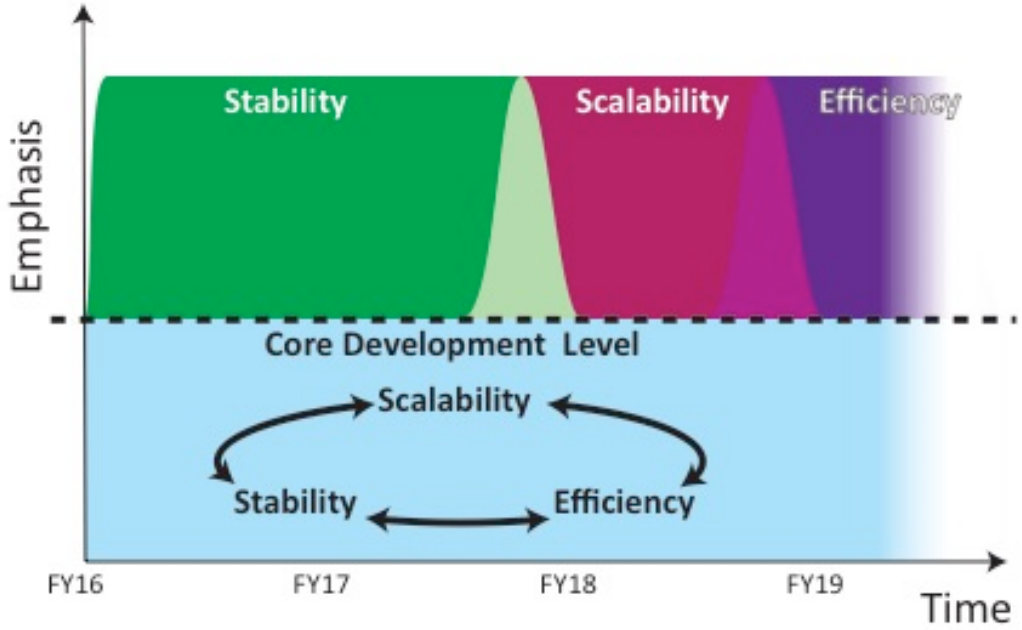
- For hybrid/halide perovskite materials as well as resulting HPSCs, connections between material, processing, properties/performance are closely linked

- Perovskites are ***cutting edge*** cell nano technology that offer ***potential*** for significant cost reductions

Approach to Pevoskite PV for SuNLaMP

- **NREL SuNLaMP program focus on three key requirements of successful PV technologies**
- **Emphasis near term is on stability (not neglecting other components)**





‣Credible applied science efforts require the ability to maintain core activities for advances in these areas with agility to change emphasis as required to advance this technology to market.

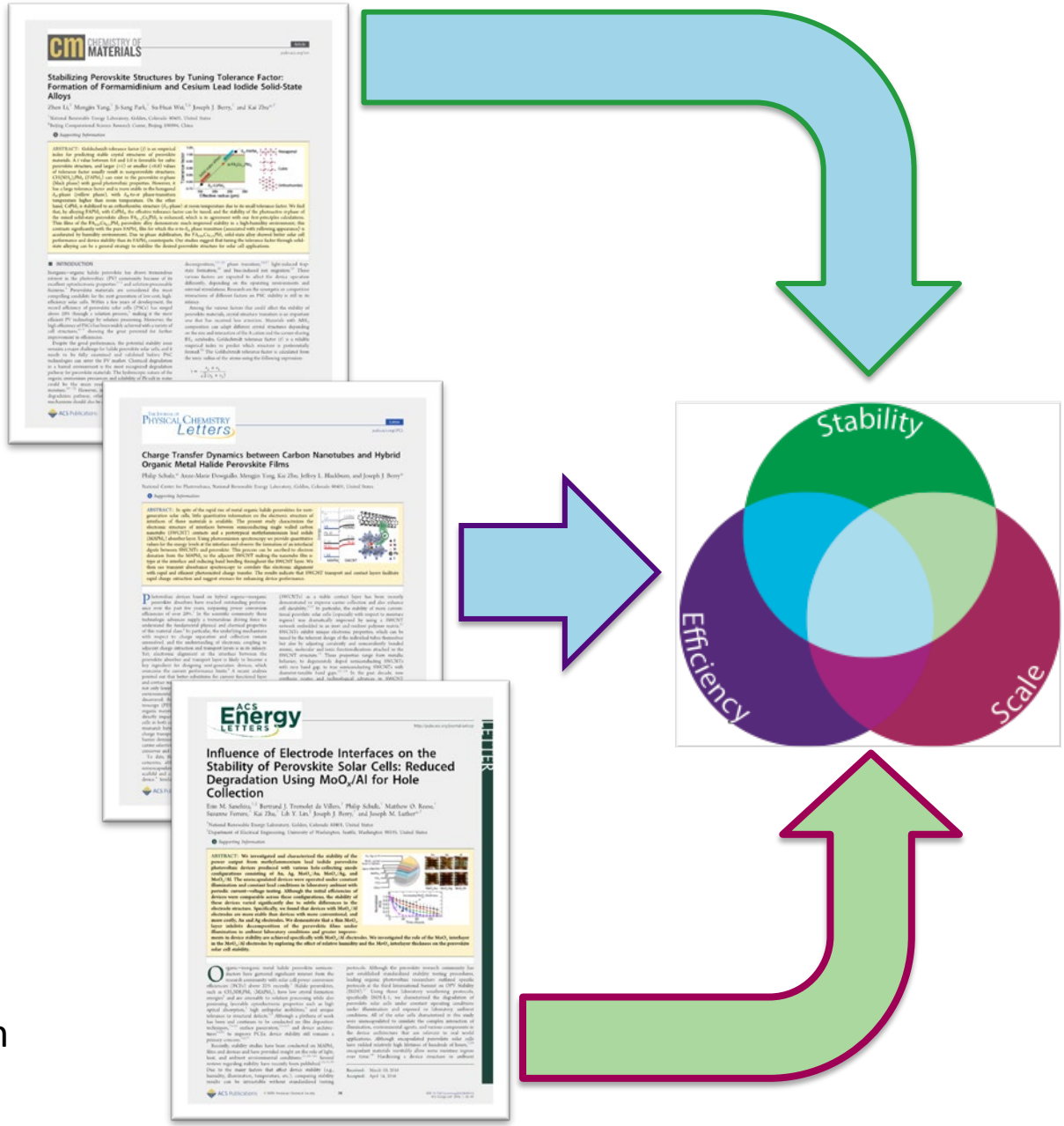
Goal: Enable HPSCs Technology

Core HPSC efforts

- Stability
  - active stability
  - +16% PAL
  - Stable in high (90%) humidity

- Efficiency and stability
  - Understanding of band alignments
  - Clearer identification of performance limitation of contacts

- Stability & scalability of devices
  - Improved stability with contact choice
  - Lower cost contact with better stability



High quality technical output is priority

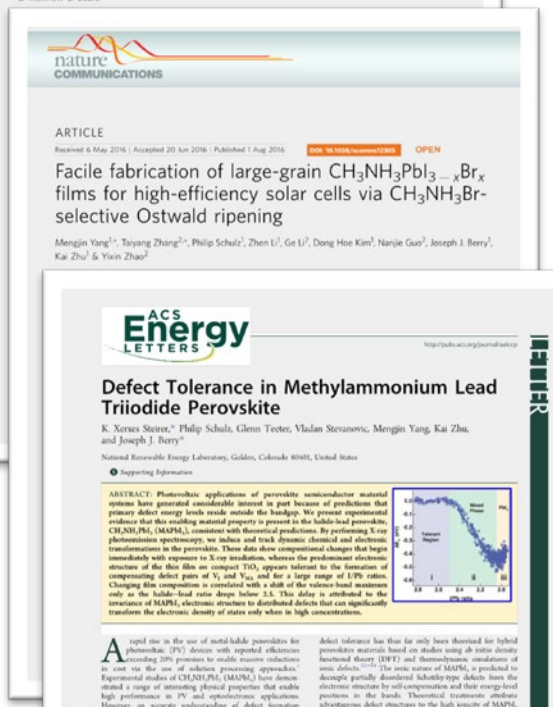
Key findings/results

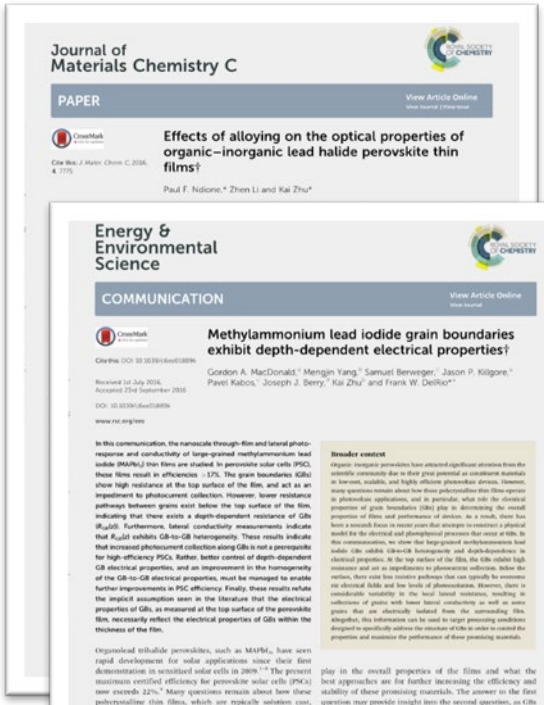
- Foundational insight into PAL material formation
- Basic information to enable interface engineering
- Critical information regarding PAL optical properties
- Demonstrate impact of contacts in HPSC device stability
- Developed & demonstrated PAL with improved hydrothermal stability
- Improved carrier transfer from PAL to SWCNT HTM and impacts on HPSCs

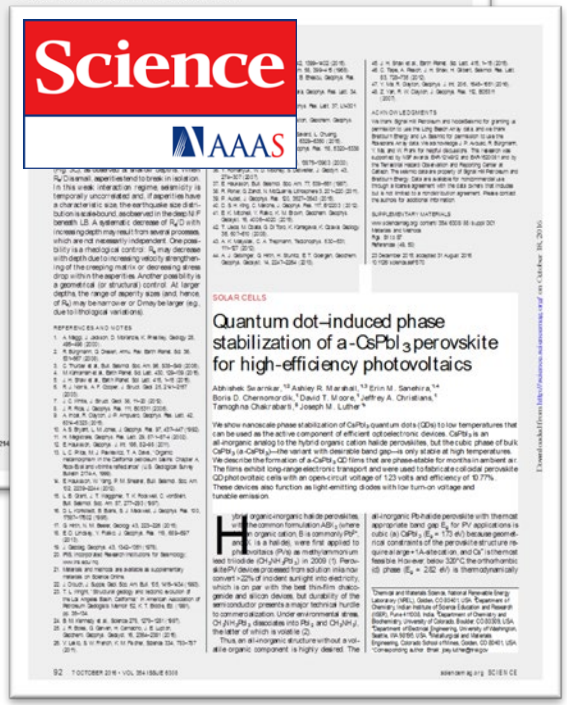
New capabilities

- Scalable processing of HPSC in development (Blade and R2R based synthesis with NREL LDRD)
- SPA capabilities (operational with additional bandwidth being constructed)

Q4FY16 publications







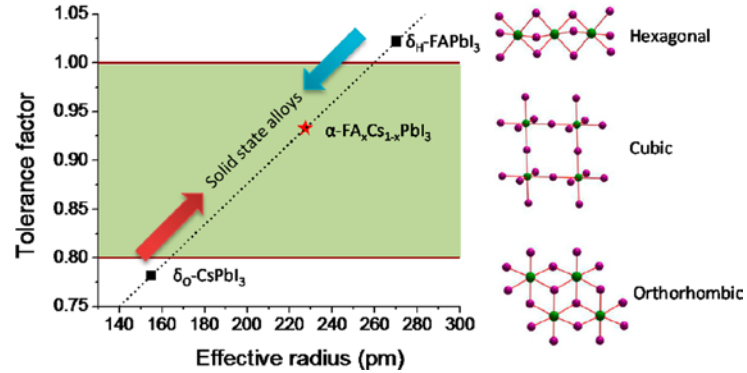
- **Additional 8 publications**
  - 4 relating to stability
  - 3 relating to scaling
  - 3 basic science innovations

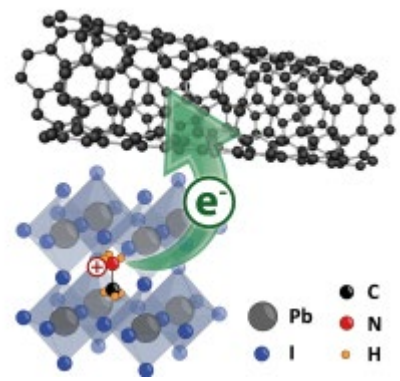
    (Multiple cross cutting publications)

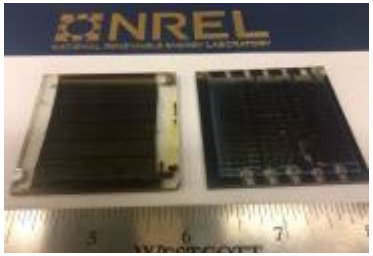
HPSC Activities

SuNLaMP activities

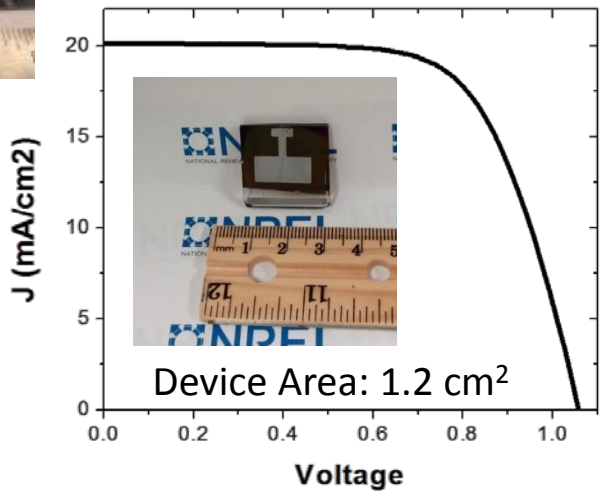
- **Performance and Stability (perovskite active layers= PAL)**
  - *$Cs_xFA_{1-x}PbI_3$ device demonstration and initial stability*
  - $Cs_xFA_{1-x}PbI_3$ microstructure control
    - Impact of structure on electronic properties
  - $MA_xCs_yFA_{1-x-y}PbBr_\alpha I_{3-\alpha}$
  - Sn based alloys
  - *Baseline studies of $MAPbI_3$*
- **Performance and Stability (interfaces and contacts)** will be discussed at ONR work shop
  - Spiro acid doping
  - Spiro–free/Alternate HTMs (organics)
  - *SWCNTs (Blackburn)*
  - $MAPbI_3$ vs Alloys Interfaces (performance and stability)
    - $Cs_xFA_{1-x}PbI_3$, $MA_xFA_{1-x}Pb\,I_3$, $MA_xCs_yFA_{1-x-y}PbBr_\alpha I_{3-\alpha}$
  - *Phosphonic acid modified interfaces (Q2 call)*
- **Scaling activities**
  - *+6 volt mini-module (Nat. Lab Day)*
  - *1cm² devices (Q2 call)*
  - Characterization and process development
  - PAL formation
- **Cross cutting studies (stability)**
  - In-operando experiments at SLAC
    - ($Cs_xFA_{1-x}PbI_3$, $MA_xFA_{1-x}Pb\,I_3$, $MA_xCs_yFA_{1-x-y}PbBr_\alpha I_{3-\alpha}$)
    - Different contacts/device architectures
  - SPA and Combi-degredation experiments
    - ($Cs_xFA_{1-x}Pb\,I_{3-}$, $MA_xCs_yFA_{1-x-y}PbBr_\alpha I_{3-\alpha}$)
    - Different contacts/device architectures
  - Materials formation







Blade coated device~13.8% PCE



Goals for SUN UP

- **Scientific publication is targeted outcome**
  - High technical merit (compelling research idea/topic)
    - Not already under investigation
  - Materials characterization based projects
  - Device characterization based projects
- **If one or both of the following is true**
    - Narrow project scope (i.e. specific technical question)
    - Existing/Prior Perovskite Material/PV experience
    - Technical Merit
  - Then 6 month term is reasonable
- **If these are not the case then it will likely take additional time to do some thing publishable**
- **Everything is negotiable but you will have to make good case for the benefits**