FORGASH STUDENT FELLOWSHIP
FINAL REPORT

FORGASH SCHOLAR:	Ilia Pavlovetc
FACULTY ADVISOR:	Masaru Kuno
REPORT PERIOD:	January 1, 2020 – December 31, 2021
PROJECT TITLE:	Cation Migration in Mixed Cation Lead Halide Perovskites Thin Films and Solar Cells
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(x) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **(x) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS:

PROPOSED A NOVEL TYPE OF SOLAR CELLS THAT EXHIBIT ENHANCED RESISTIVITY TO AN UNWANTED EFFECT OF CATION MIGRATION. RESULTS WERE PUBLISHED IN ONE OF THE TOP SOLAR ENERGY RESEARCH JOURNALS (ACS ENERGY LETTERS) AND PROVIDED NEW INSIGHTS INTO CATION MIGRATION IN PEROVSKITE SOLAR CELLS. THE FINDINGS ARE ALSO IN PREPARATION FOR SUBMISSION AS AN INTELLECTUAL PROPERTY (IP).

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Establish collaboration	Collaboration between ND and NREL established	100
Published paper	Manuscript prepared and published	100
Prepare IP	In preparation by ND Idea center	25-75

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	None
EXTERNAL AWARDS	None
JOURNAL ARTICLES	"Suppressing Cation Migration in Triple-Cation Lead Halide Perovskites", Ilia M. Pavlovetc, Michael C. Brennan, Sergiu Draguta, Anthony Ruth, Taylor Moot, Jeffrey A. Christians, Kyle Aleshire, Steven P. Harvey, Stefano Toso, Sanjini U. Nanayakkara, Jonah Messinger, Joseph M. Luther, and Masaru Kuno, ACS Energy Lett. 2020, 5, 9, 2802–2810
BOOKS AND CHAPTERS	None
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	1. SPIE Photonics West 2020, San Francisco, 1–6 February 2020, "Super resolution infrared photothermal microscopy: operating principle and detection limits", I. M. Pavlovetc. 2. MRS Fall 2020 (Virtual), November 27-December 4 2020, "Suppressing Cation Migration in Triple-Cation Lead Halide Perovskites", I. M. Pavlovetc. Future conferences: 3. SPIE Photonics West 2021, Virtual, 6 - 11 March 2021, "Infrared photothermal microscopy beyond life sciences: applications in materials science", I. M. Pavlovetc 4. MRS Spring 2021, (Virtual or Seattle), April 18-23 2021, "Title: TBD", I. M. Pavlovetc
AWARDS, PRIZES, RECOGNITIONS	None
INTERNAL COLLABORATIONS FOSTERED	Yanliang Zhang, Notre Dame Aerospace and Mechanical Engineering, High throughput printing and spectroscopy of novel perovskite solar cells. (A future collaboration as a spinoff of Forgash project)
EXTERNAL COLLABORATIONS FOSTERED	Joey Luther, National Renewable Energy Laboratory, Assistance with time-of-flight secondary ion mass spectroscopy (TOF-SIMS measurements. Solar cells preparation and stability testing).
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

MAJOR GOALS AND ACCOMPLISHMENTS

(Additional Details, Technical Results, Charts and Graphics)

Mixed cation and anion $APbX_3$-type lead halide perovskites (A^+=Cs^+, CH_3NH_{3+} [MA^+], or $(NH_2)_2CH^+$ [FA^+]; X^-=Br^- or I^-) have received extensive attention for use as cheap, efficient light harvesters in solar cells. However, issues regarding their long-term stability represent an unresolved problem which ultimately prevents their commercialization. While most of the stability studies focus on external effects such moisture or heat, electric field induced ion migration is a relatively unstudied phenomenon which represents an intrinsic instability of these solar cells. For instance, cation migration induces current-voltage hysteresis, perovskite material deterioration, and overall attrition of solar cell performance. My work, therefore, is focused on exploring, understanding, and suppressing electric-field induced cation migration in $FA_xMA_yCs_{1-x-y}PbI_3$ perovskite thin films and solar cells.

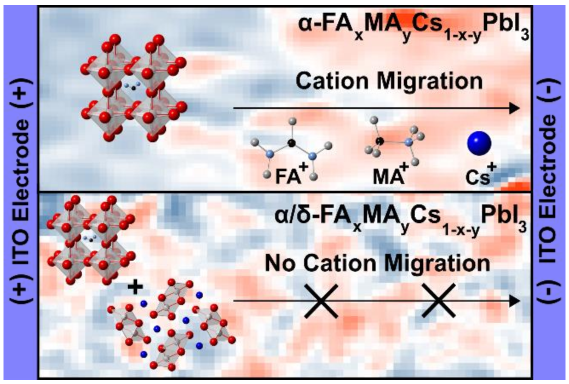

Fig. 1. Cation migration as imaged by IR-PHI at Notre Dame. Top panel – cations do migrate and accumulate at negative electrode. Bottom panel – no significant changes in cation distribution is observed.

In order to do that, I studied a whole compositional range of $FA_xMA_yCs_{1-x-y}PbI_3$ perovskites, with *x* and *y* range from 0 to 1. What I found was that some of the studied compositions formed a nonuniform alloys that exhibited interesting electronic properties. By conducting X-ray diffraction measurements, I found that they are made of mixture of α-phase $FAPbI_3$ and δ-phase $CsPbI_3$ perovskite materials. Then, to survey the relative stabilities of single (α) and mixed-phase (α/δ) perovskites against cation migration, I used a recently developed, super-resolution infrared imaging technique called infrared photothermal heterodyne imaging (IR-PHI). The measurements pointed to the greater stability of α/δ alloys against cation migration relative to their α-phase counterparts (**Figure 1**).

These findings were further corroborated by our collaborators at the National Renewable Energy Laboratory (NREL), where they used spatially resolved time-of-flight secondary ion mass spectrometry (ToF-SIMS) to image cation movement in different perovskite compositions. Similar to IR-PHI measurements, ToF-SIMS experiments demonstrated that in α-phase perovskite materials all cations do accumulate at corresponding negative electrode. In contrast to α-phase perovskites, mixed α/δ alloys showed no evidence of cations migration.

Important step of this work was to demonstrate that the resistance to cation migration in materials itself is translated into solar cells operational stabilities. For that purpose, our collaborators at NREL manufactured α-$FA_{0.76}MA_{0.15}Cs_{0.09}PbI_3$ and α/δ-$FA_{0.33}MA_{0.33}Cs_{0.33}PbI_3$ planar solar cells. Then, by conducting solar cell stability tests we found that average power conversion efficiency (PCE) for α-phase solar cells drop to 35% of their initial value within ~200 hours. At the same time, PCE for α/δ-phase solar cells drop only to 50% on the same time scale. In other words, immediate improvements in long-term stability on the order of 20% was achieved.

To conclude, this work demonstrated that cation migration is mitigated in α/δ-phase perovskites. Importantly, this resistance to cation migration translates into improved solar cell device operational stability of α/δ-phase solar cells.

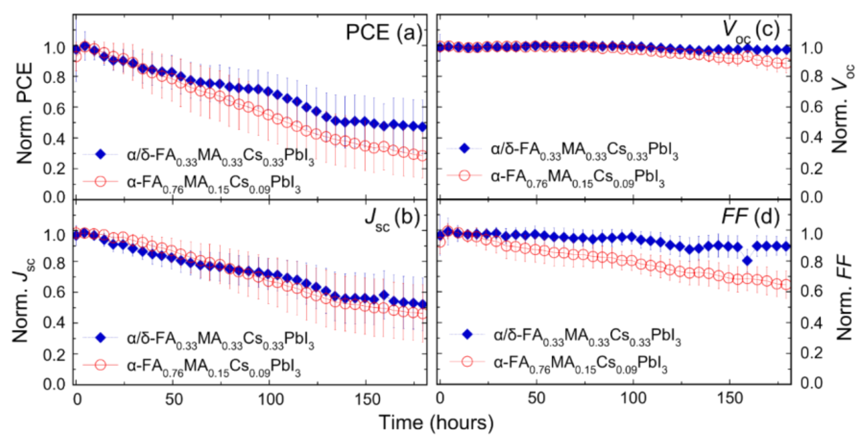

Fig. 2. Solar cells characteristics: (a) PCE, (b) short-circuit current (J_{SC}), (c) open circuit voltage (V_{OC}), and (d) fill factor (FF) for α-$FA_{0.76}MA_{0.15}Cs_{0.09}PbI_3$ (red circles) and α/δ-$FA_xMA_yCs_{1-x-y}PbI_3$ (blue diamonds) solar cells over ~200 hours of simulated solar illumination.