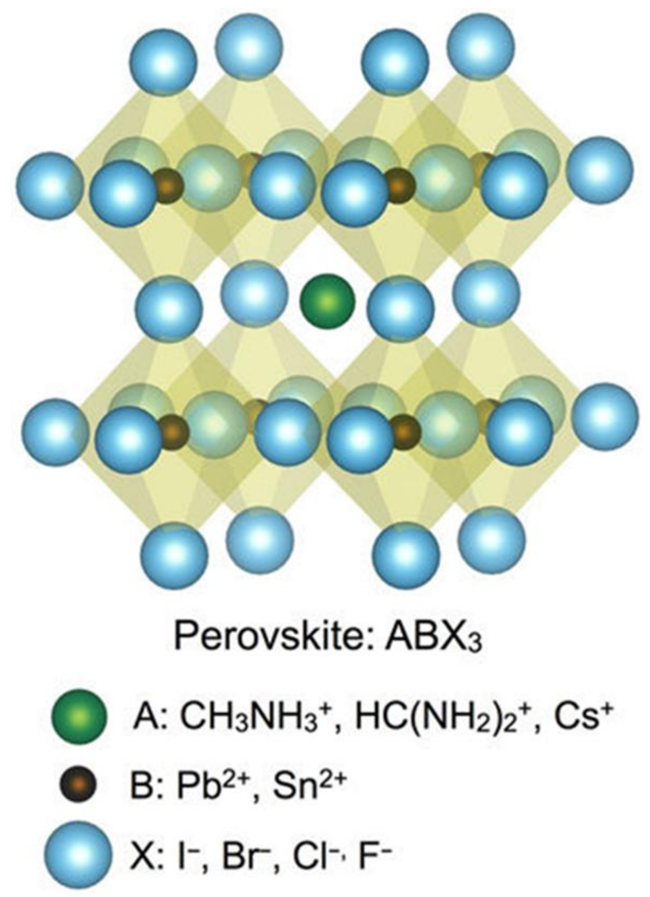
The Goldilocks Combination to Unprecedented Perovskites

Maegyn Grubbs[1], Bong Lee, Ph.D.[2], Zygmunt Gryczynski, Ph.D.[2], Sergei Dzyuba, Ph.D.[1], and Jeff Coffer, Ph.D.[1]
Texas Christian University
1. Department of Chemistry and Biochemistry
2. Department of Physics and Astronomy

I. Introduction

Metal-halide perovskites are crystalline semiconductive materials with a tunable direct bandgap, defect tolerance, and high charge carrier mobility. These useful properties have led to application perovskites such as LEDs, solar cells, and more recently lasers. In this project, cetyl ionic liquid (IL) enhanced Methylammonium Lead Tribromide perovskites thin films were studied on substrates with varying refractive indices to determine how refractive index impacts photophysical properties. Methylammonium Lead Tribromide perovskites have a refractive index of 2.19. In comparison glass, a common substrate, has a refractive index of 1.51 while yttrium-stabilized zirconium oxide (YSZ) is 2.15.

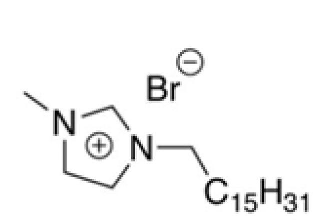


IL= Ionic Liquid
MA= Methylammonium
"Perovskite" = $MAPbBr_3$

Thin films of Methylammonium Lead Tribromide grown on yttrium-stabilized zirconium oxide (YSZ) in the presence of an ionic liquid are found to be strongly emissive in the green at a wavelength of 535 nm (with quantum efficiency values above 60%). The associated photoluminescence excitation (PLE) spectra show an unprecedented series of distinct peaks, one set with an average energy separation of ~200 milli-electron volts, the other set with a ~100 milli-electron volt separation indicating possible Giant Rashba Splitting. The preparation and structure of these films, along with origins of this splitting, are presented.

II. Experimental

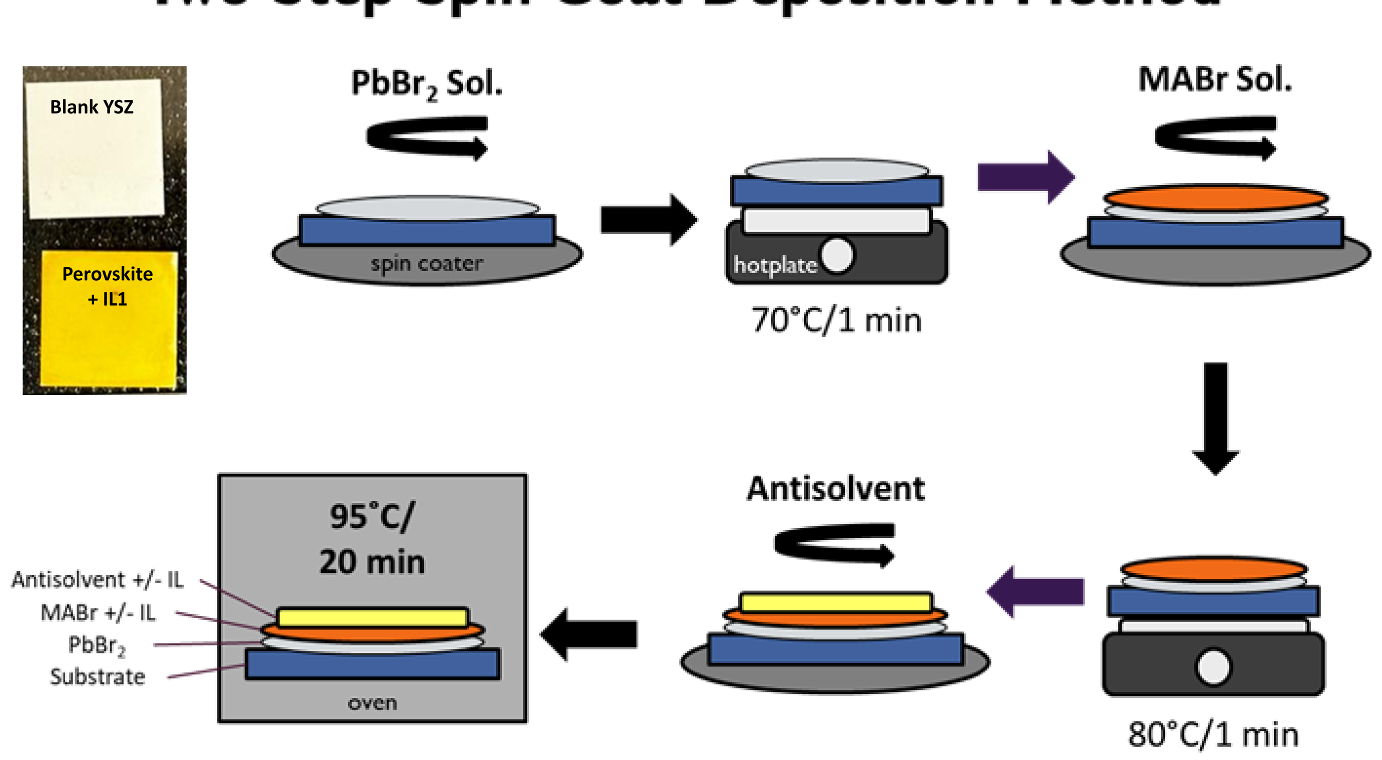
IL1



$[C_{16}$-mim]Br
Imidazolium

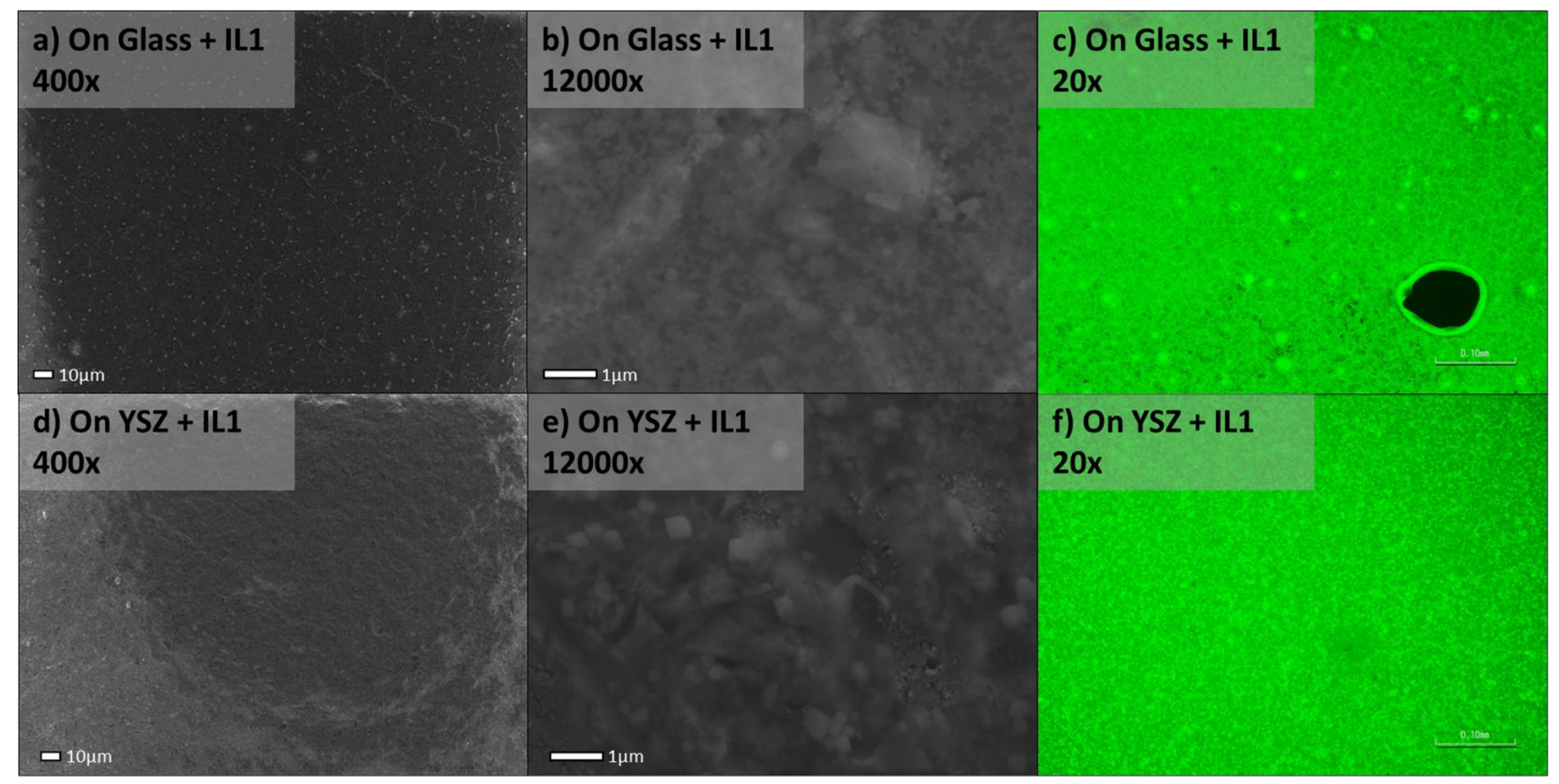
Material	Refractive Index
$MAPbBr_3$	2.19
Glass	1.51
Yttria-stabilized Zirconia (YSZ)	2.15

Two-Step Spin Coat Deposition Method



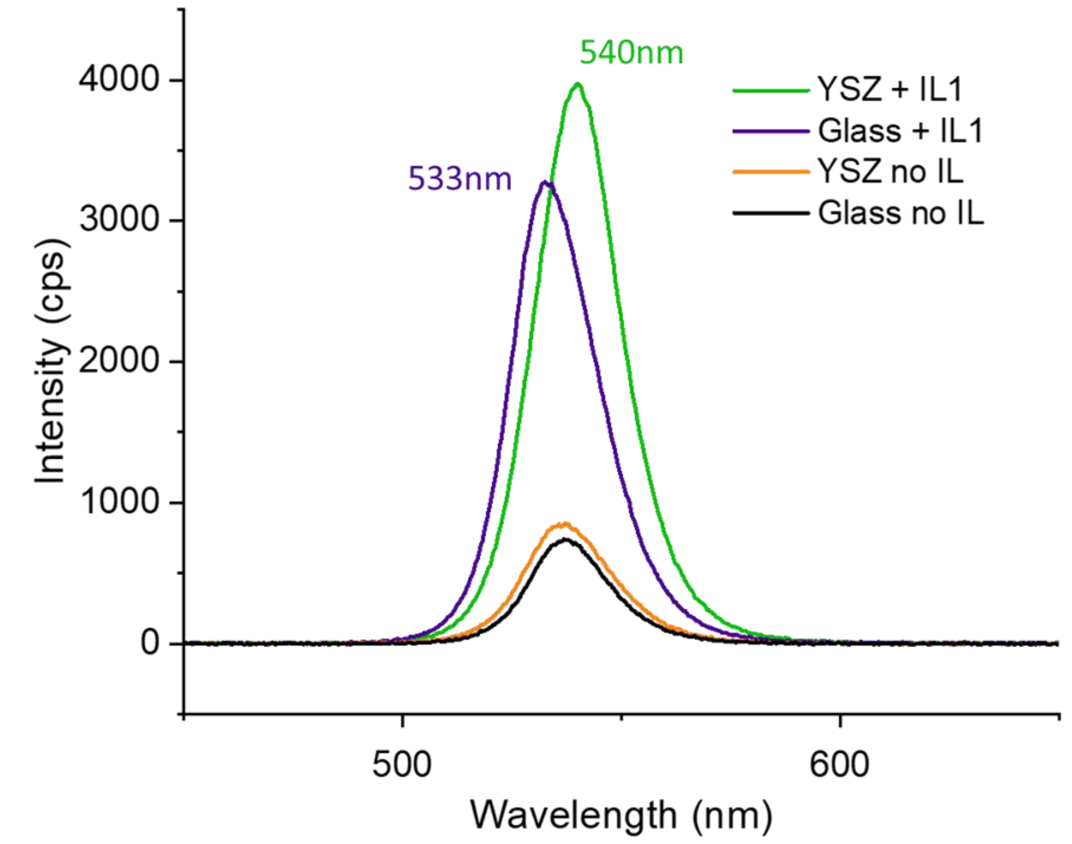
III. Results

Figure 1- Scanning Electron Microscope (SEM) and Photoluminescent (PL) images



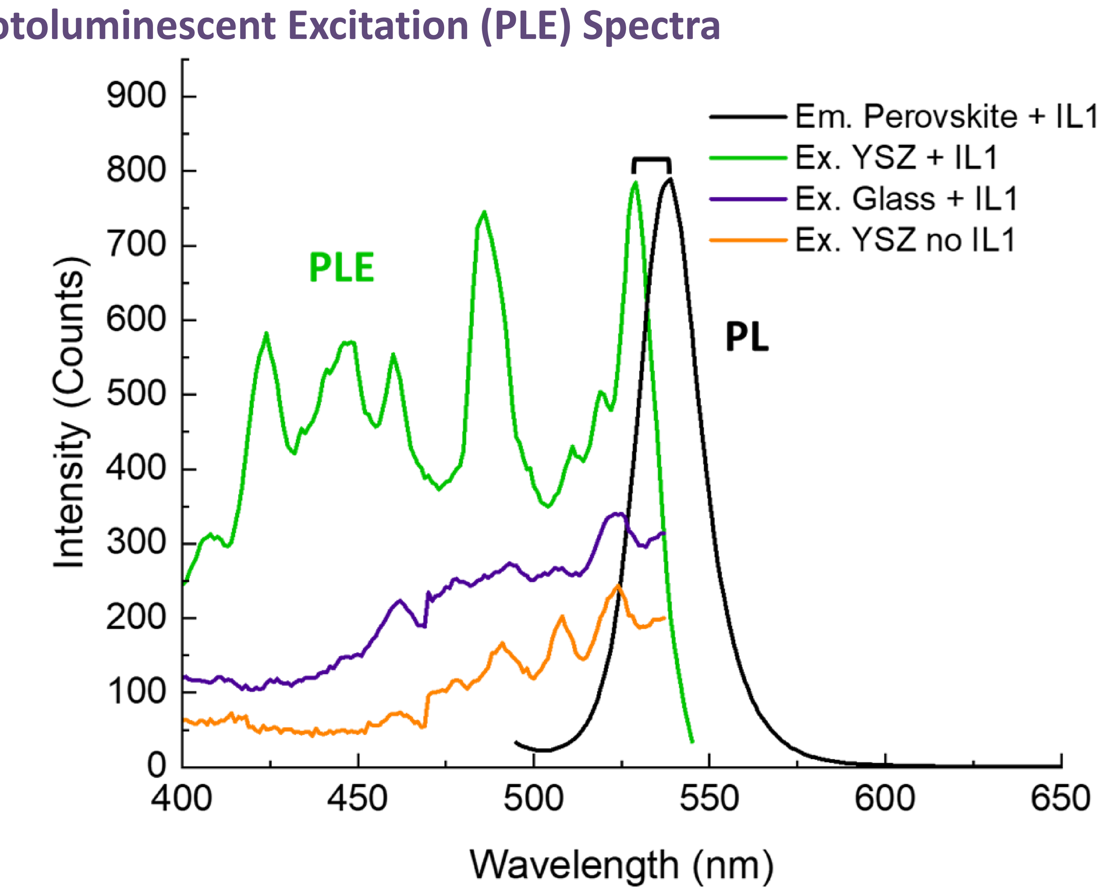
- Both substrates resulted in perovskite thin films with textured morphologies and bright green photoluminescence.

Figure 2- Photoluminescence (PL) Spectra



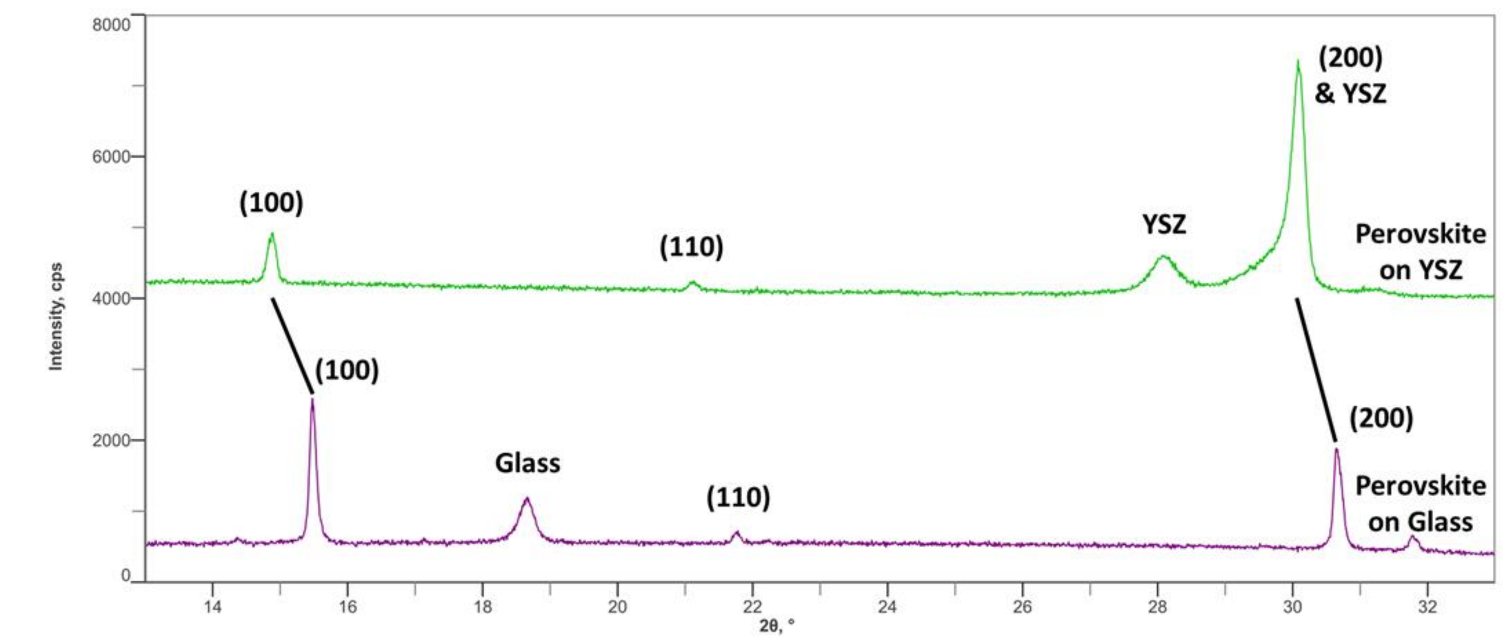
- Perovskite + IL1 thin films on YSZ were higher in photoluminescence intensity (brighter) than the thin films grown on glass or without IL1. (excitation= 370nm)

Figure 3- Photoluminescent Excitation (PLE) Spectra



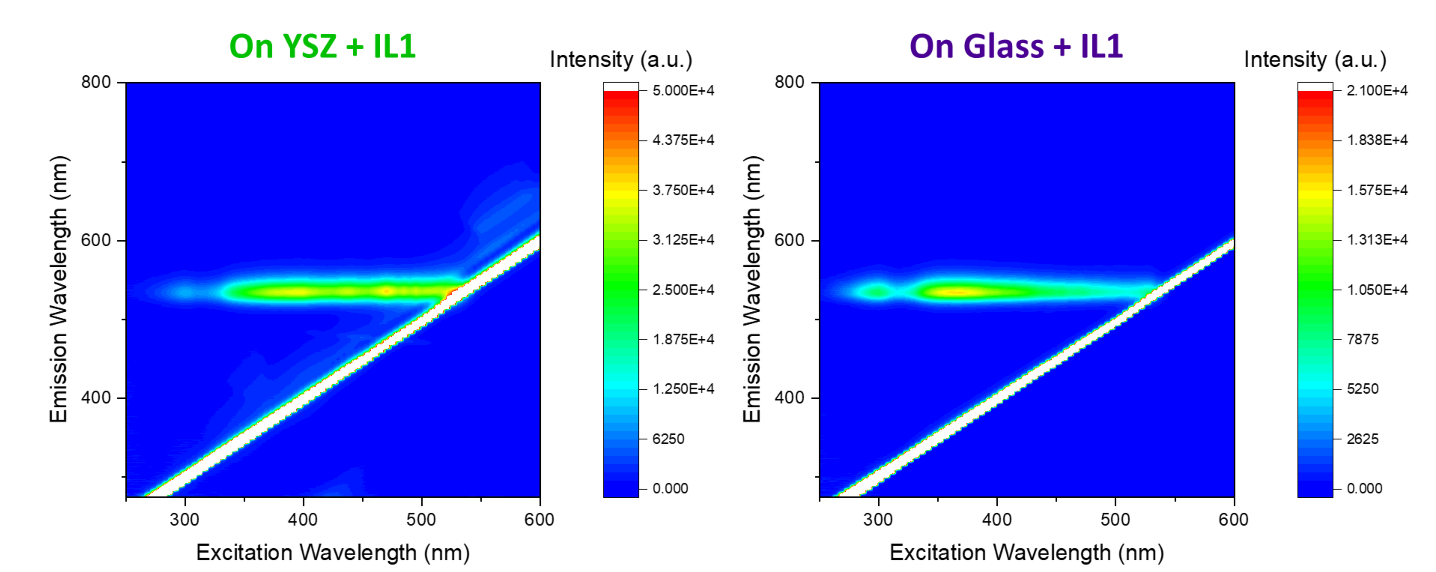
- Perovskite + IL1 thin films on YSZ have a unique fine excitation structure that is not seen in the thin films grown on glass or without IL1 (Goldilocks Combination). Additionally, the perovskite thin films have a small stoke shift (0.04eV).

Figure 4- Powder X-ray Diffraction (XRD)



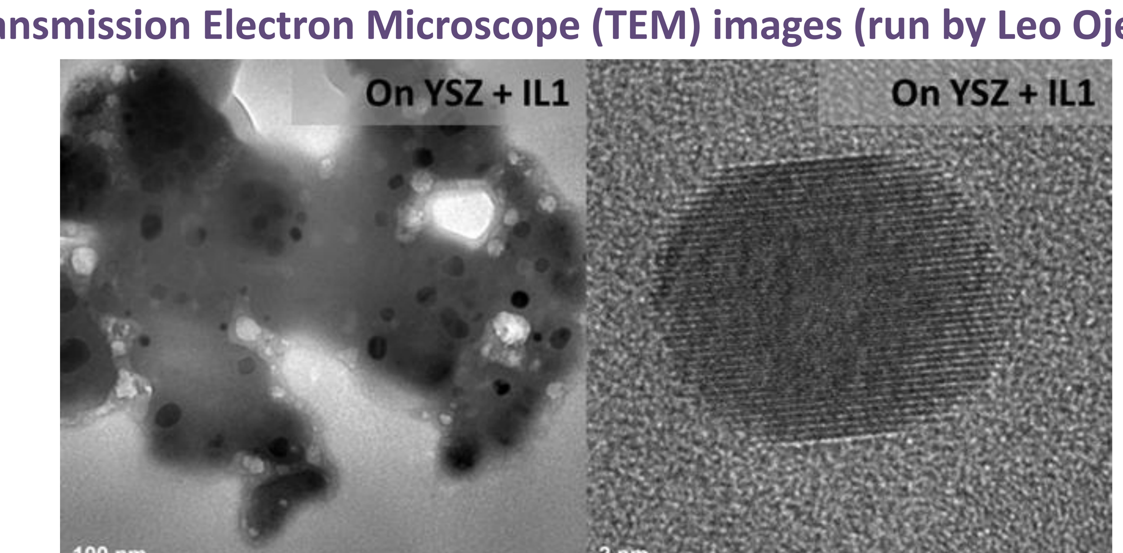
- Perovskite + IL1 on YSZ has a lower angle shift for the cubic $MAPbBr_3$ XRD peaks indicating a difference in lattice spacing compared to the perovskite + IL1 on glass thin film.

Figure 5- Excitation-Emission Matrix (EEM)



- Perovskite + IL1 on YSZ EEM pattern reflects the distinct PLE peaks

Figure 6- Transmission Electron Microscope (TEM) images (run by Leo Ojeda Hernandez)



- Selecting for the smallest particles, TEM showed the perovskite size is too big for strong quantum confinement (<5nm)

IV. Discussion

- Perovskite thin films with IL1 are brighter than control films without IL and the films grown on YSZ have a higher intensity over the films grown on glass
- Perovskite + IL1 on YSZ thin films are in the cubic phase according to XRD but the peaks are shifted which resulted in a difference in the d spacing, indicating a change in the crystal lattice spacing
- A unique fine PLE structure was present in only perovskite thin films made on YSZ with IL present
- Confirmed not to be due to strong quantum confinement (<5nm) by TEM

V. Future Work

- Film thickness will be measured via SEM cross section
- Photoluminescence Quantum Efficiency (PLQE) will be measured for all films to compare efficiency
- Perovskite thin films with IL1 on YSZ could be applied as the emitting layer in a laser

VI. References

1. Metal Halide Perovskites For Light-Emitting Diodes. *Nature Materials* **2021**, *20*, 10-21
2. Ionic Liquids-Enabled Efficient and Stable Perovskite Photovoltaics: Progress and Challenges. *ACS Energy Letters* **2021**, *6*, 1453-1479
3. Defect Tolerance and Intolerance in Metal-Halide Perovskites. *Advanced Energy Materials* **2020**, *10* (37), 2001959

VII. Acknowledgments

- TCU Department of Chemistry and Biochemistry