

## **NDnano Undergraduate Research Fellowship (NURF) 2015 Project Summary**

**1. Student name:** Tessa Ronan

**2. Faculty mentor name:** Prof. Prashant V. Kamat

**3. Project title:** Coordination Chemistry of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  Perovskite Precursor Solution

**4. Briefly describe any new skills you acquired during your summer research:** As a physics graduate in a chemistry lab, there are many new skills that I have acquired during my research here. The other postgraduate students working in the lab were very helpful and at hand to show me anything I needed to know. I learned how to calculate and weigh out required volumes and concentrations of solutions as well as how to filter the solutions. I also learned how to deal with any waste in the lab, such as sharps and acids, or any toxic materials. The most useful techniques I learned were coordination chemistry, UV-vis spectroscopy and photolysis. I also learned how to make and test solar cells.

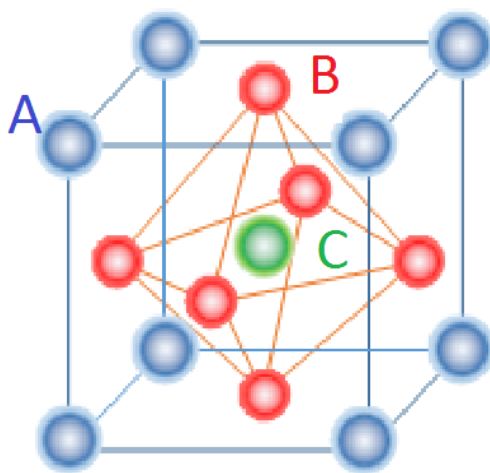
**5. Briefly share a practical application/end use of your research:** The studies carried out by me will be continued after I leave with the aim to understand the crystallization process of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite structure and to subsequently improve the solar cell performance.

**Begin two-paragraph project summary here (~ one type-written page) to describe problem and project goal and your activities / results:**

Metal-halide perovskites are emerging as top contenders for light absorption in solar cell technologies. In the past four years, the perovskite solar cell power conversion efficiencies have risen from 3% to over 20%, indicating their potential to overtake the silicon based solar technologies currently on the market. The perovskite crystal structure is made up of an organic halide cation (A), a metal halide cation (B), and a halide anion (X) in an  $\text{ABX}_3$  structure. This work focuses primarily on the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite. The precursor solutions display inverse


solubility in gamma-Butyrolactone, which enables the rapid growth of single crystals. However their exact growth mechanism from solution is still unknown. Through UV-vis absorption spectroscopy, my aim was to explore the complexation that occurs in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  precursor solutions and what the effect of temperature, stoichiometry, solvent, deaeration, and irradiation has on the crystallization process, and subsequently on the solar cell performance.

By measuring the absorption spectroscopy of the precursor solution at higher temperatures, it was found that increasing temperature weakens the complexation of lead iodide. By varying stoichiometries of iodide to lead, it was found that with excess ligand, the higher coordination complexes of lead iodide dominate. Samples of  $\text{CH}_3\text{NH}_3\text{I}$  were irradiated using a Xenon lamp, in which case the solution turned from clear to yellow to brown over time. Attributing this process to be the dissociation of iodide under UV light, further investigations were carried out on the effect of irradiation on different complexations of iodide and lead iodide. A pre-irradiated precursor  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution was used in the fabrication of solar cell electrodes. These electrodes had, on average, a higher current density output than the control cells. If consistent, further studies will be required to analysis why, and to investigate what the optimal irradiation parameters will be to potentially improve the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cell performance.



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Publications (papers/posters/presentations):



### Coordination Chemistry of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Precursor Solution

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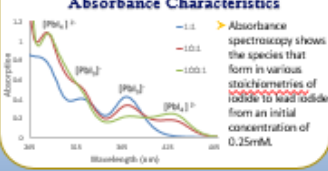


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#### Introduction

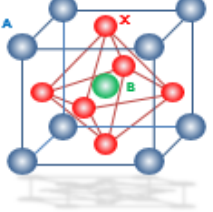
- Metal-halide perovskites are emerging as top contenders for light absorption in solar cell technologies. In the past four years, the perovskite solar cell power conversion efficiencies have risen from 3% to over 20%, indicating their potential to overtake the silicon based solar technologies currently on the market.
- The precursor solutions display inverse solubility in gamma-Butyrolactone (GBL), which enables the rapid growth of single crystals. However their exact growth mechanism from solution is still unknown.

#### Absorbance Characteristics



Absorbance spectroscopy shows the species that form in various stoichiometries of iodide to lead iodide from an initial concentration of 0.25mM.

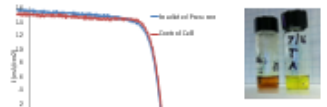
#### Abstract



The perovskite crystal structure is made up of an organic cation (A), a metal cation (B), and a halide anion (X) in an  $\text{ABX}_3$  structure. This work focuses primarily on the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite. Through UV-vis absorption spectroscopy, this work aims to explore the complexation that occurs in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  precursor solutions and what the effect of temperature, stoichiometry, solvent, and irradiation has on the crystallization process, and subsequently on the solar cell performance.

#### Solar Cell Performance using a Pre-Irradiated Precursor Solution

A  $\text{CH}_3\text{NH}_3\text{PbI}_3$  precursor solution in a mixture of DMF and DMSO was irradiated at  $297\text{mW/cm}^2$  for 25 minutes using a Xenon lamp, turning it from yellow to brown. The solution was spin coated onto the substrate using the 1-step Lewis Adduct fabrication method. A Fill Factor as high as 82% was achieved.



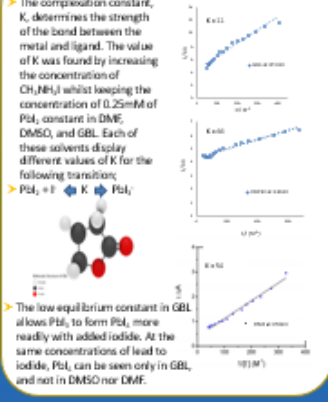
Average	Efficiency %	J (mA/cm <sup>2</sup> )	Voc (V)	FF
Irradiated Precursor Solution Cell	13.8 ± 0.35	12.3 ± 0.37	1.20 ± 0.05	0.83 ± 0.06
Control Cell	13.8 ± 1.50	13.0 ± 1.13	1.20 ± 0.05	0.78 ± 0.09

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#### Complexation in Different Solvents

The complexation constant,  $K_c$ , determines the strength of the bond between the metal and ligand. The value of  $K_c$  was found by increasing the concentration of  $\text{CH}_3\text{NH}_3$  whilst keeping the concentration of  $\text{PbI}_2$  constant in DME, DMSO, and GBL. Each of these solvents display different values of  $K_c$  for the following transition:

$\text{PbI}_2 + \text{I}^- \rightleftharpoons \text{K} \rightleftharpoons \text{PbI}_3^-$



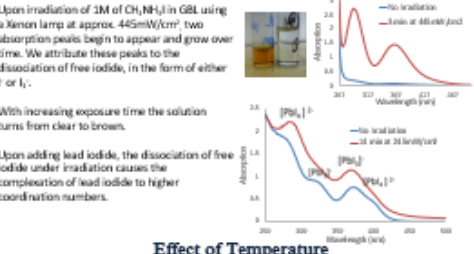
The low equilibrium constant in GBL allows  $\text{PbI}_2$  to form  $\text{PbI}_4$  more readily with added iodide. At the same concentrations of lead to iodide,  $\text{PbI}_4$  can be seen only in GBL, and not in DMSO nor DMF.

#### Effect of Irradiation on the Precursor Solution

Upon irradiation of 3M of  $\text{CH}_3\text{NH}_3$  in GBL using a Xenon lamp at approx.  $445\text{mW/cm}^2$ , two absorption peaks begin to appear and grow over time. We attribute these peaks to the dissociation of free iodide, in the form of either  $\text{I}^-$  or  $\text{I}_2$ .

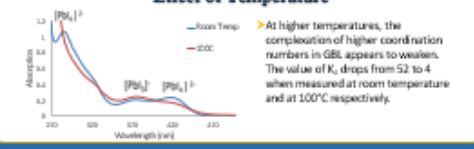
With increasing exposure time the solution turns from clear to brown.

Upon adding lead iodide, the dissociation of free iodide under irradiation causes the complexation of lead iodide to higher coordination numbers.



#### Effect of Temperature

At higher temperatures, the complexation of higher coordination numbers in GBL appears to weaken. The value of  $K_c$  drops from 52 to 4 when measured at room temperature and at  $100^\circ\text{C}$  respectively.



#### Crystallization

One of the most attractive features of perovskites is how easy it is to grow single crystals. At a concentration of 3M, a single seed  $\text{CH}_3\text{NH}_3\text{PbI}_3$  crystal begins to appear in GBL within 15 minutes of being heated to  $150^\circ\text{C}$ .

#### Conclusions and Future Work

By varying stoichiometries, the higher coordination complexes of lead iodide dominate.

Increasing temperature weakens the complexation of lead iodide.

$\text{CH}_3\text{NH}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  both dissociate upon irradiation in GBL, in which case the solution turns from clear to brown over time. Attributing this process to be the dissociation of iodide into  $\text{I}^-$  or  $\text{I}_2$ , and lead iodide into metallic lead, further investigations are required to study the effect of irradiation on the complexation of lead iodide in different solvents.

A pre-irradiated precursor  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution was used in the fabrication of solar cell electrodes. These electrodes had, on average, a higher current density output than the control cells. Further studies will be required to investigate what the optimal irradiation parameters will be to potentially improve the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cell performance.

Visit [www.KamatLab.com](http://www.KamatLab.com) for more information about the group

