

**Development of Organometallic Hybrid Perovskite
Single Crystals towards Radiation Sensing and
Optoelectronic Applications**

A Dissertation Presented for the
Doctor of Philosophy
Degree
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ABSTRACT

Organometallic hybrid perovskites have shown great promise for many optoelectronic applications, such as photovoltaics, LEDs, photodetectors, lasing etc. Recently, single crystalline OMHP has been demonstrated as a cost-effective alternative to traditional, expensive inorganic semiconductors. In this perspective, MAPbBr₃ [Methylammonium lead tribromide] single crystals are focused towards development in efficient high-energy radiation detection. The growth, effects of growth conditions, device fabrication, and application results are presented here to discuss the challenges and solutions of these challenges for the material to be capable of high resolution radiation sensing. Inverse temperature crystallization techniques have been demonstrated as a simple growth method for high quality MAPbBr₃ single crystals. The ability to alter the growth conditions, such as precursor ratio and purity, to enhance the electronic properties of MAPbBr₃ single crystals is experimentally demonstrated, with bulk resistivity values up to $1 \times 10^{10} \Omega$ and trap densities on the order of $10^8 - 10^9 \text{ cm}^{-3}$. The importance of electrode selection and interfacial engineering for improved performance is also discussed, where a Cr electrode gives a high interfacial resistance of $1.79 \times 10^9 \Omega$, compared to the low interfacial resistance of Au contacts giving a much lower interfacial resistance of $1.32 \times 10^7 \Omega$. The main challenge in this material is described by the imbalance of electron and hole charge transport properties. Doping of Cl⁻ is discussed in literature and experimentally demonstrated here to improve the electron transport in MAPbBr₃-based single crystals, via alpha particle radiation detection. Results to radiation sensing of alpha particles, gamma photons, and neutrons show promising results for MAPbBr₃ single crystals as a novel, cost-effective radiation sensing material under $\$10 \text{ cm}^{-3}$.

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Introduction

Accurately detecting ionizing radiation (high energy radiation) is a vital application in terms of nuclear security. High performance radiation sensors have many challenges that create operational limitations. Currently, high resolution materials (classified as $<1\%$ energy resolution at 662 keV) are very high cost due to synthesis or operational conditions. For instance, CdZnTe (CZT) is a high-resolution detection material that is currently used, but the material is expensive ($\sim 3000 \text{ cm}^{-3}$) due to high material processing through High Pressure Bridgman growth techniques.¹ HyperPure Germanium (HPGe) is also a high resolution standard used; however, these detectors operate at extremely high voltages ($\sim 3000 \text{ V}$ bias) and must be cooled to temperatures lower than 100 K during operation. Therefore, HPGe detectors are also very expensive and bulky which limits them for widespread development.² LaBr₃ scintillators have also shown decent energy resolution (3% at 662 keV) at room temperature. However, these materials are still relatively expensive ($\sim 400 \text{ cm}^{-3}$).³ Because of these challenges in current high-energy radiation sensing, it is vital to provide wider-spread development of radiation sensing materials at much lower costs. This can be achieved by lowering cost of high-resolution materials, improving efficiency of lower cost materials, or by introducing new, low-cost, high-resolution radiation sensing materials.

To answer these current challenges in high-energy radiation sensing materials, single crystalline organometallic halide perovskites (OMHPs) are proposed for gamma-ray sensors and sensing of other high-energy radiation. These materials have already shown to

be produced at very low costs ($\sim \$4\text{-}10\text{ cm}^{-3}$) and are operational at room temperature. The key to developing this material will focus on high-quality crystals for gamma-ray sensing at high resolution ($\leq 1\%$ at 662 keV) with large-scale volumes ($> 1\text{ cm}^{-3}$).

1 Organometallic Hybrid Perovskites

In this chapter, a detailed literature review will be presented on relevant topics including an overview on OMHPs in section 1.1. Then, in section 1.2, single crystalline OMHPs will be reviewed and compared to thin film counterparts.

1.1 General Literature Overview

Synthesis of OMHPs was first reported by Weber in 1978, who fabricated the cubic perovskite structure by mixing precursors of CH_3NH_3 , concentrated Br_2 and $\text{Pb}(\text{NO}_3)_2$ under stirring at 100°C .⁴ In the last decade, OMHPs have gained widespread attention in a variety of optoelectronic applications. Research in OMHP solar cells has shown promising advancement towards next generation photovoltaic materials.⁵ First reports of OMHP solar cells began in 2009, when a liquid-based dye-sensitized solar cell, using methylammonium lead halide (MAPbX_3) as an active layer, produced a power conversion efficiency (PCE) of around 3-4%.⁶ After only a short period of 4 years, PCEs for OMHP solar cells increased to over 15%.⁷⁻⁸ Due to the rapid progress of perovskite solar cells, editors of *Science* and *Nature* selected this material as one of the biggest scientific breakthroughs of 2013.⁹⁻¹⁰ Keeping up with this trend, the most recent recorded PCEs for OMHP solar cells have already consistently reached over 20%, with a record of 23.3% in 2018.¹¹ Research in photodetectors has shown that OMHPs are also promising materials with comparable performances to commercially available silicon and III-V photodetectors.¹² Recent advances have also been made for light-emitting diode (LED) applications based on OMHP

materials.¹³ Studies have shown unprecedented performances with maximum luminance values up to 91,000 cd/m^2 and external quantum efficiencies over 11.7%.¹⁴⁻¹⁵ OMHPs have also gained attention in lasing applications due to tunability of emission and room temperature operation for low threshold lasing.¹⁶ Also, research has shown that this class of perovskite can also perform as room temperature gas sensors,¹⁷ resistive switching memory devices,¹⁸ and thermoelectric device.¹⁹ Pertaining to the specific work of this dissertation, OMHPs have also shown great promise as low-cost, room-temperature, ionizing radiation sensors including detection of x-rays, gamma-rays, neutrons and alpha particles.²⁰⁻²²

1.2 OMHP Crystal Structure

Based on these applications, OMHPs have many appealing optoelectronic properties that allow for efficient performance. OMHPs have a very unique crystal structure with hybrid components, as shown in Figure 1.1. The organic cation, A, (i.e., methylammonium, formamidinium, etc.) creates a structural template for solution processing. The metal cation, B, (i.e., Pb^{2+} , Sn^{2+} , etc.) lies at the center of an octahedral cluster BX_6^{-4} , where A is in 12-fold cuboctahedral coordination with the halide atoms, X, (i.e., Cl^- , Br^- , I^-).²³⁻²⁴ The crystal structure's formability and stability can be estimated by the Goldschmidt factor as shown in Equation 1.1,²⁵ where r_A , r_B , and r_X are the ionic radii for the A and B cation and the X anion, respectively. The octahedral factor, $\mu = \frac{r_B}{r_X}$, is also used to evaluate the perovskite structure stability.

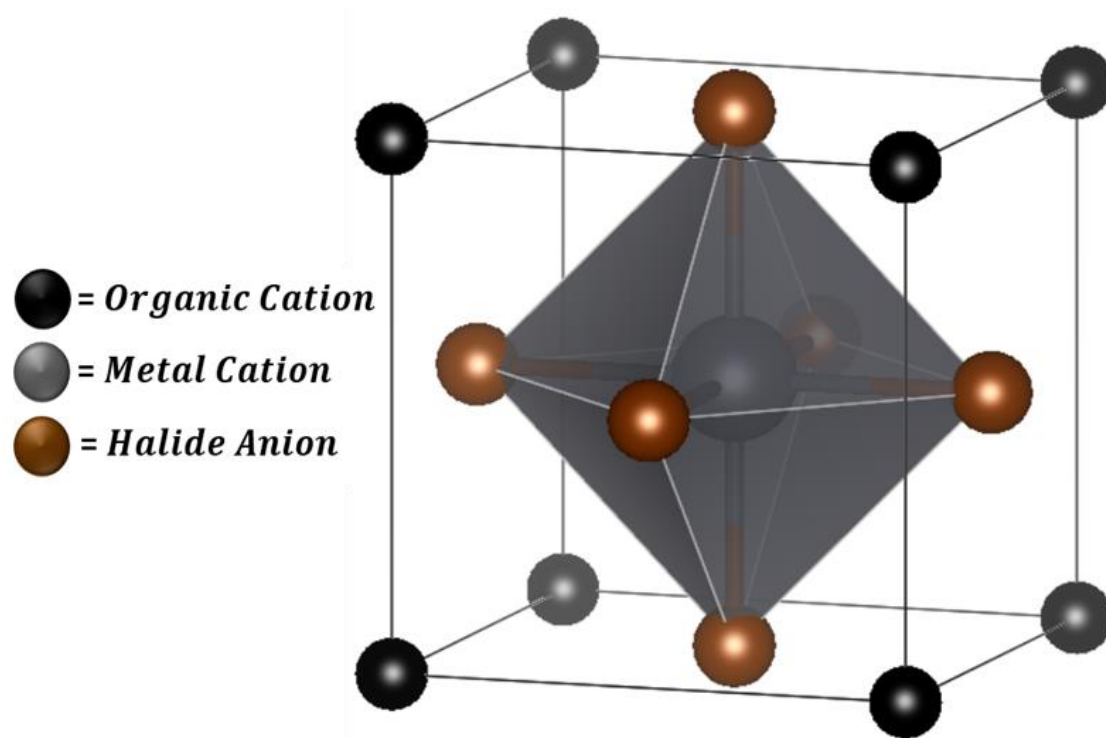


Figure 1.1. General schematic for perovskite crystal structure of OMHPs showing positions for organic, inorganic and halide atoms.

It is shown that the perovskite crystal structure is stable when $0.813 \leq t \leq 1.107$ and $0.442 \leq \mu \leq 0.895$.²⁶

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1.1)$$

This unique, hybrid crystal structure gives OMHPs many attractive intrinsic properties for opto-electronic applications. First, beneficial optical properties for these materials are of great importance including high absorption coefficients ($>10^4 \text{ cm}^{-1}$),²⁷ which has given great attention to OMHPs as photovoltaic materials, wide absorption range (band edge ranging from 425-760 nm), which shows promise for application in photodetection, as well as tunable bandgaps (1.5-3 eV),²⁸ displaying tunability for applications in lasing and other electronic applications. Next, OMHPs have many important electronic properties for applications including low exciton binding energies ($<50 \text{ meV}$),²⁹ which allows for easy room temperature operation, long electron and hole diffusion lengths ($>1 \text{ }\mu\text{m}$),³⁰⁻³¹ which shows that trapping in this material does not hinder charge transport, high ambipolar charge mobilities ($\sim 100 \text{ cm}^2/\text{V} \cdot \text{s}$),³²⁻³³ essential for charge collection efficiencies, and extended charge carrier lifetimes (microseconds),³⁴ which shows that charge recombination is less probable. Another large advantage of OMHPs are their simple, low-cost processing. Thin film OMHPs are typically prepared using cost-effective, chemical and physical deposition techniques including one and two-step solution spin-casting, vapor deposition, and vapor-assisted solution deposition, which are desirable techniques to fabricate devices for a variety of applications.³⁵⁻³⁷

1.3 Optoelectronic Properties of OMHPs

Of all these attractive properties of OMHPs, the focuses herein for understanding fundamental processes for this material class will heavily lie in the photoluminescence, (PL) tunable bandgaps, and properties of excited states. A schematic showing the mechanisms of photoluminescence is shown in Figure 1.2. PL occurs when a material absorbs photons of energy equal to $h\nu_1$ from any source of electromagnetic radiation, shown in step 1. When the material absorbs the incident photon, an electron is excited to a higher energy level in the atom, shown in step 2. Then, in step 3, vibrational relaxation occurs to the lowest energy level in the conduction band. Finally, in step 4, the electron relaxes back to the valence band (VB) ground state. During this relaxation process, the energy gained from relaxation is emitted as a photon equal to energy $h\nu_2$. The photoluminescent properties are largely dependent on the band gap of a material, as the band gap is the minimum energy of photoexcitation required to excite an electron from the valence band to the conduction band (CB). The band gap also determined the energy gained via the relaxation process. Therefore, tuning the band gap of this material class allows for control over photoluminescence and absorption properties for desired applications. In Figure 1.3., PL spectra are shown for varying compositions of OMHPs.³⁸ Here, it is shown by simply modifying the halide composition of MAPbX_3 , large changes are seen in the PL and absorption properties towards tuning the bandgap of the material. This material class has become of great interest in lasing, LEDs, photodetectors, and photovoltaics due to the simple substitution technique providing a wide range of bandgaps, as shown in Figure 1.3.

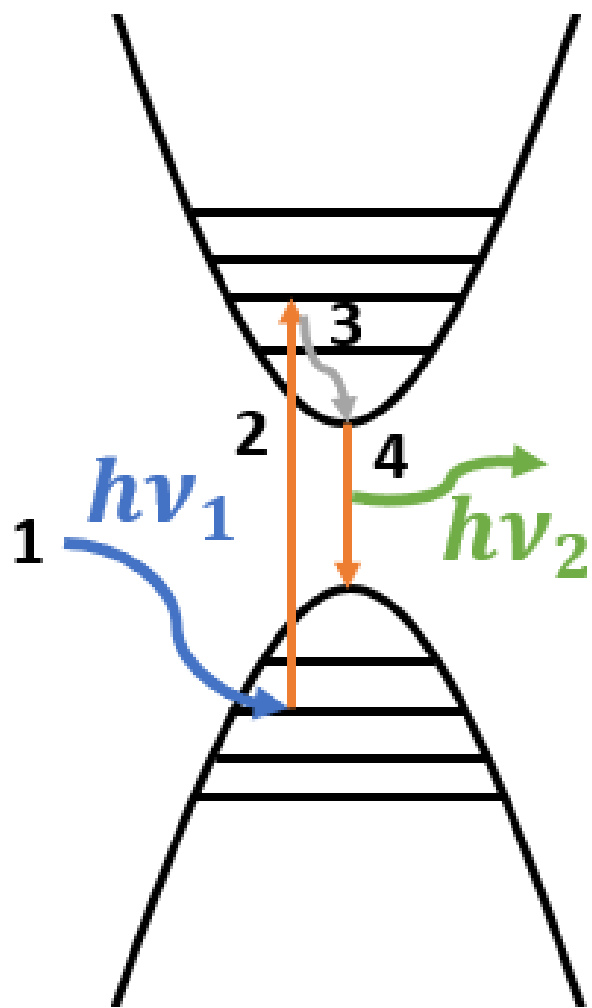


Figure 1.2. Step-by-step schematic of photoluminescence mechanism.

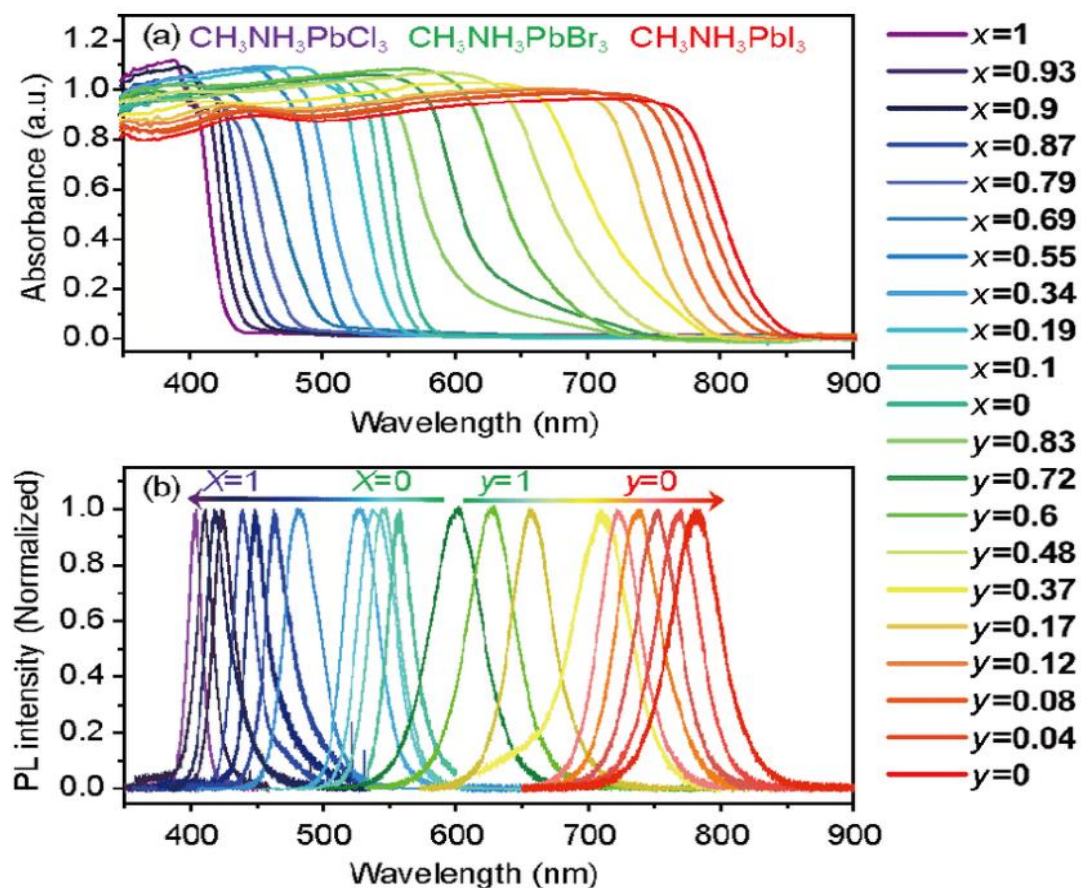


Figure 1.3. Using anion substitution for chemical composition of OMHP for (a) tunable absorption band edges to demonstrate tunable bandgaps and (b) tuneable photoluminescent properties. Reproduced from ref. 38 with permission. Copyright 2017 Science China Chemistry.

In lasing and LEDs, the tunable band gap allows for a variety of emission wavelengths between 400 and 800 nm to provide a variety of colors. In photodetectors and photovoltaics, the tunable band gap allows for a variety of absorption edges to tune the wavelengths of absorbable light. These changes in bandgap are also be of importance in high energy radiation sensing.³⁹ In high energy radiation detection, an incoming photon must ionize electrons and excite them to higher energy levels across the bandgap of the material. Smaller bandgaps can help by incident photons from radiation sources creating a large amount of charge. On the other hand, if the bandgap is too small, (such as $E_g(\text{HPGe}) = 0.67 \text{ eV}$) thermal excitation processes can cause high leakage currents creating too much electronic noise. Higher band gap materials have higher resistivities, allowing them to operate at room temperature. Therefore, OMHP materials give a unique tunability to bandgap to find the optimal condition for efficient sensing performance. PL has also been used as a useful tool to understand the differences between surface and bulk excited states and recombination mechanisms. A one-photon and two-photon excitation method has been widely used to probe OMHPs for surface and bulk characteristics, respectively. Using one-photon excitation, the wavelength of excitation light is readily absorbed and only one photon is needed to create an excited state. However, in two-photon excitation, the wavelength is much larger than the luminescence wavelength. Because of this, the energy of the incident photoexcitation is much weaker. Therefore, two photons are needed to create an excited state.

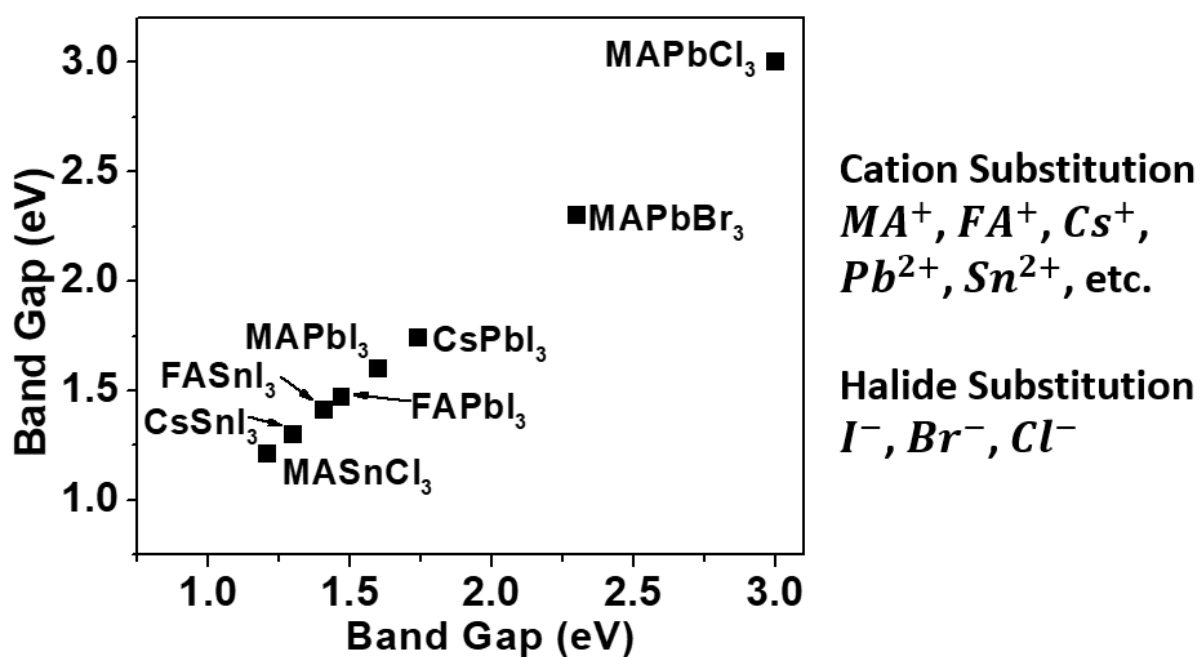


Figure 1.4. Experimental band gaps for different elemental compositions of OMHPs showing the wide range of tunability.

In Figure 1.5., it is shown that using a photoexcitation source with double the wavelength of an absorbed wavelength (two-photon) can penetrate through the material, while exciting bulk states. Meanwhile, because the absorption coefficient of OMHPs is so high, the shorter, absorbed wavelengths for photoexcitation are readily absorbed at the surface and cannot penetrate through the material to excite bulk states. Using this method has been a key advancement in discerning recombination mechanisms and charge transfer in the bulk and surface, leading towards a deeper understanding of these complex material properties. From Figure 1.5, it is shown that when probing the bulk with two-photon excitation, there is a shift in photoluminescence wavelength for both MAPbBr₃ and MAPbI₃, as compared to the one-photon excitation.⁴⁰ This shows an integral problem that needs to be addressed for single crystalline OMHPs where the surface quality is lower than the bulk and more trapping and defects exist in the surface than in the bulk.

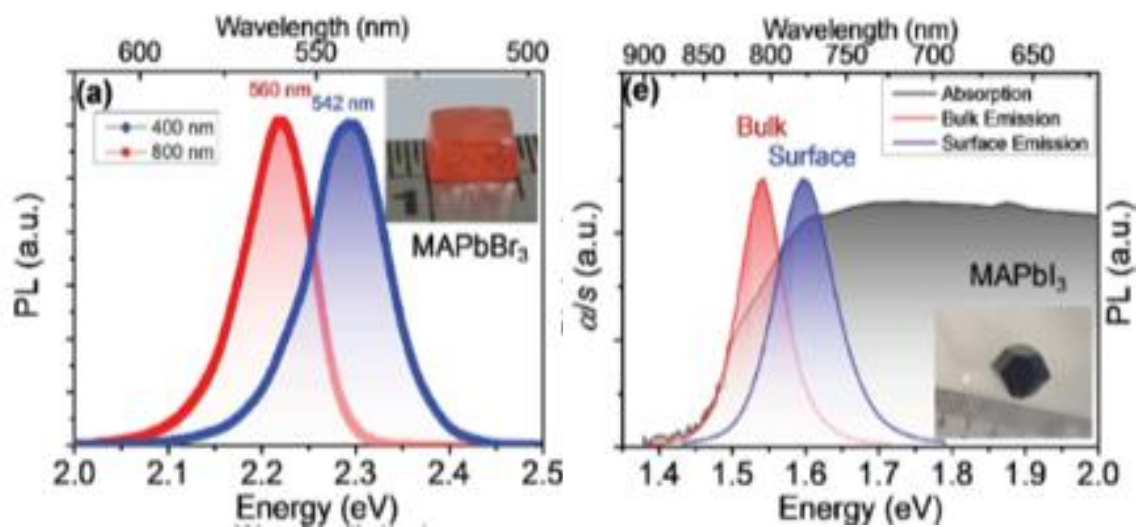


Figure 1.5. PL emission spectra with one-photon and two-photon photoexcitation for (Left) MAPbBr₃ and (Right) MAPbI₃ single crystals. Reproduced from ref. 40 with permission. Copyright 2016 Advanced Materials Energy.

Lastly, it is essential to understand the mechanisms that control excited states in OMHPs. Figure 1.6. depicts how charge is created and travels through OMHP active layers. First, an excitation energy interacts with the OMHP active layer by absorption of photons via visible light or ionizing interaction methods via high-energy radiation. Once the charge is created from the incident excitation, an electron is excited from the valence band to the conduction band of the active layer. These excited states can either exist as free e-h pairs (~70%) or excitons, (~30%) which is a bound e-h pair. Because the exciton dissociation energy is so low (< 50 meV), they can readily dissociate on the order of picoseconds at room temperature.⁴¹ Once charge is dissociated, the charge carrier lifetime can be as high as the order of microseconds to milliseconds, depending on the composition and structure of the film or single crystal. The energy barrier for electrons and holes to recombine is larger than the dissociation energy of excitons, estimated to be ~ 90 meV, and is thermally activated due to dipole moments associated with MA^+ cations that need to be aligned properly.⁴² Therefore, recombination can be controlled when it is not desirable for applications, such as photovoltaics and radiation sensing to enhance the performance of devices. This also encourages long charge diffusion lengths with long carrier lifetimes, desirable for high charge collection efficiencies (CCE) in solar cells and sensing applications. The properties for excited states are of great importance for different applications, and tunability of these mechanisms has been of great interest for OMHPs.

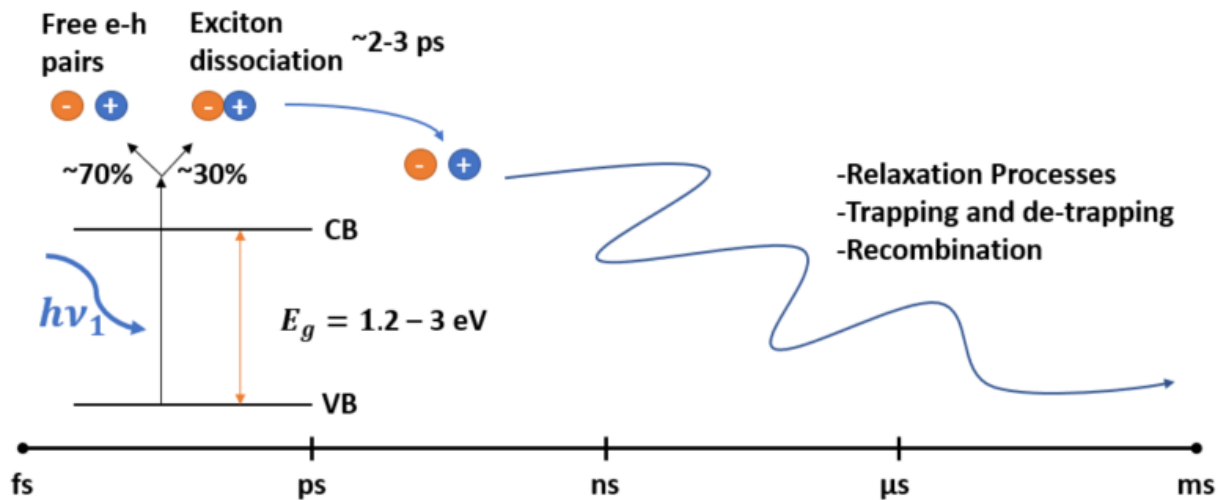


Figure 1.6. Schematic representation of charge generation, excitation and collection mechanisms in OMHPs.

1.4 Single Crystalline OMHPs

Single crystalline OMHPs have gained increasing attention in recent years. Compared to thin films, single crystals hold many advantages for fundamental understanding and applications. Benefits to studying single crystalline materials include the lack of morphologies and disordered grain boundaries, which allows for deeper understanding into intrinsic properties of OMHP materials. For devices, the ability to synthesize high quality, pure, large volume crystals is beneficial for many optoelectronic and sensing applications. In 1999, Mitzi *et al.* first reported the successful synthesis of perovskite single crystals at room temperature using a layered solution approach to grow $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$ single crystals.⁴³ Recently, high quality bulk single crystals with high purity, less grain boundaries and grains, and low defect density have emerged with a few popular growth methods. Many growth methods have been developed for OMHP single crystals. Here, a short review is provided to understand the advantages and disadvantages of all the different growth techniques studied. Common single crystal growth techniques can be separated into categories including solid growth, vapor growth, melt growth, and liquid growth. Solid growth is typically used for metals and rare earth materials via straining and annealing of polycrystalline masses. In vapor growth, common techniques include physical vapor deposition (PVD), such as sputtering and thermal evaporation, and chemical vapor deposition (CVD) techniques, involving a chemical reaction between a transporting agent and crystallization material through a hot zone to a crystallization zone.

1.5 Crystallization Thermodynamics

Crystal growth is the process of producing a crystal (solid phase) from a liquid or gas phase. Crystallization consists of two important parts, nucleation and crystal growth. Crystallization must first begin with nucleation, then crystal growth occurs to grow larger crystals via successive layers on top of the original nucleation point, also known as a seed crystal. Nucleation occurs when solute molecules in a solvent begin to gather into clusters, and once these clusters reach a critical size, form a stable nucleus. The critical size is determined by many different factors including temperature, supersaturation, solubility, etc. Atoms in the nucleus arrange in a specific, periodic manner, which is known as the crystal structure. Once the nucleus is formed, it becomes a seed, which facilitates larger crystal growth. Nucleation or crystal growth may be the predominant process, depending on the conditions, which can dictate crystal size. This is important to control the crystal size. Crystallization can also be explained in more detail through a thermodynamic approach. Here, understanding the energy processes that drive crystallization is essential to perform successful crystal growth.

Primary nucleation occurs as the first step of crystal growth, as explained above. This process can occur homogeneously or heterogeneously. Homogeneous nucleation is not influenced by any other solids, such as the walls of the crystallization vessel or any foreign particles. Meanwhile, heterogeneous nucleation occurs when foreign substances cause an increase in nucleation rate. Heterogeneous nucleation is most common, as homogeneous nucleation requires a substantial amount of energy to begin. Most crystal growth processes

can be modeled using the equation of Gibbs free energy (ΔG) at constant temperature and pressure, described by Equation 1.2,

$$\Delta G = \Delta H - T_E \Delta S = 0 \quad (1.2)$$

where ΔH is the enthalpy (total heat) of the system, T_E is the equilibrium temperature, and ΔS is the entropy (degree of disorder or randomness) of the system. This equation can then be simplified to Equation 1.3.

$$\Delta S = \frac{\Delta H}{T_E} \quad (1.3)$$

It is important to note that although the process of crystallization decreases entropy, the formation of the crystal is exothermic, so the second law of thermodynamics is still conserved.⁴⁴ Nucleation is described by Equation 1.4,⁴⁵

$$B = \frac{dN}{dt} = k_n (c - c^*)^n \quad (1.4)$$

where B is the number of nuclei formed per unit volume, N is the number of nuclei per unit volume, k_n is a rate constant dependent on the solute's solubility in the solvent, c is the instantaneous concentration of solute, c^* is the solute concentration at saturation, and n is an empirical exponent dependent on the system. Here, $(c - c^*)$ is the supersaturation of the solute in solvent. From these equations, it is shown that there are many parameters that must be accurately controlled for precise crystallization including solubility of solute in the solvent of choice, solubility limits for supersaturation, and temperature, which also influences solubility.

1.6 OMHP Single Crystal Growth Techniques

For the perovskite class of materials, single crystal growth methods have mainly focused on melt and liquid growth techniques. Melt growth, specifically the Bridgman technique, has been employed to grow a well-developed CsPbBr_3 single crystal. A schematic is shown in Figure 1.7 for the Bridgman growth technique.⁴⁶ In the Bridgman growth technique, a melt is prepared for the desired compound to be crystallized. The melt is placed in a sealed ampoule under vacuum, which is then placed in a furnace. Inside the furnace, there is a hot zone in the top and a cold zone at the bottom. The ampoule is placed in a support tube and fixed to a lifting platform. The lifting platform then slowly moves the melt from the hot zone to the cold zone. The melt solidifies into its final single crystal as the ampoule passes through the cold zone. In Figure 1.7, the perovskite example of CsPbBr_3 is shown, as grown by the Bridgman technique.⁴⁶⁻⁴⁷ The Bridgman growth technique provides many advantages for high quality single crystal growth. First, the size of the crystals grown are only limited by the size of the ampoule the single crystal is grown in. Therefore, it is simple to create crystals of desired sizes for a variety of application requirements. Another advantage of this crystal growth technique is that there is precise control over the system parameters during growth. In this perspective, temperature of the hot and cold zone, velocity of the lifting platform, and melt composition are some of the parameters that allow precise control over the system. However, the system does have disadvantages as well. One main disadvantage to this technique is growth time. Typically, this growth technique takes weeks to months depending on the melt compound.

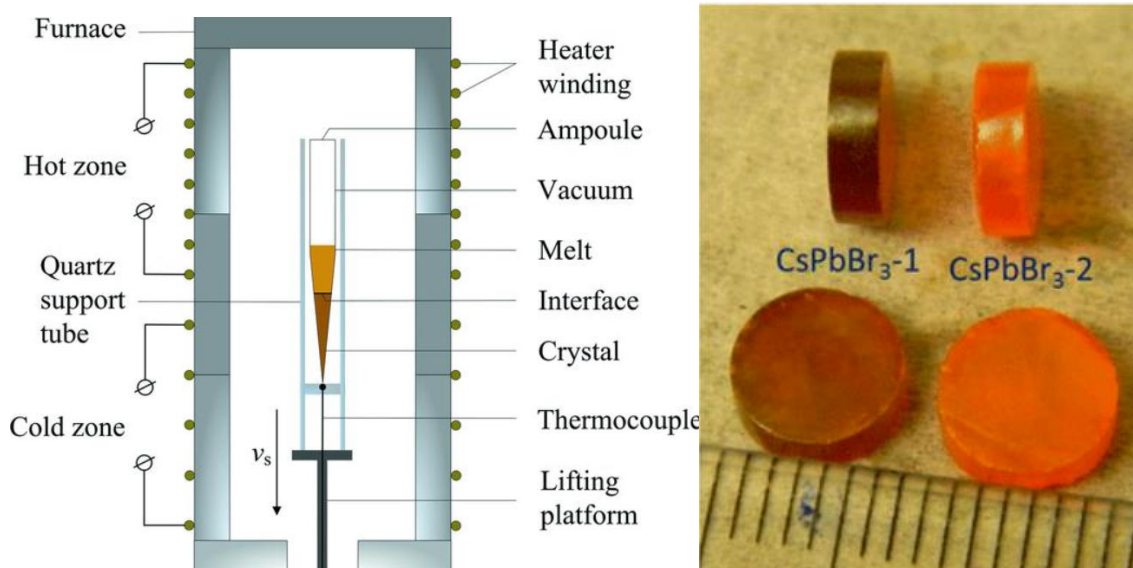


Figure 1.7. (Left) Schematic of Bridgman crystal growth technique. Reproduced from ref. 44 with permission. Copyright 2017 Journal of Applied Crystallography. (Right) CsPbBr_3 single crystals grown with Bridgman technique using commercially available PbBr_2 ($\text{CsPbBr}_3\text{-1}$) and freshly precipitated PbBr_2 ($\text{CsPbBr}_3\text{-2}$). Reproduced from ref. 45 with permission. Copyright 2013 Crystal Growth & Design.

Time and expense of the system both make the technique relatively high cost. In addition, the melt Bridgman growth requires that the melt compound has a single melting temperature. While this technique has been used successfully for many compounds and inorganic perovskite, CsPbBr_3 , the requirement for a single melting temperature prevents OMHPs from being grown with this method. Because of this, solution growth techniques have been widely studied to grow high quality OMHP single crystals. The common solution-based growth techniques include, top-seeded solution growth (TSSG) method,⁴⁸ antisolvent vapor-assisted crystallization (AVC) method,⁴⁹ and the inverse temperature crystallization (ITC) method.⁵⁰⁻⁵¹ Figure 1.8 (left) shows a schematic diagram of the TSSG method for growing MAPbI_3 single crystals, as shown in Figure 1.8 (right).⁴⁸ This method is a two-step process. The first step of this process involves precipitation of small MAPbI_3 crystals. In this step, lead(II) acetate trihydrate is mixed in hydroiodic acid (HI) using an oil bath at 100 °C. Once the lead(II) acetate trihydrate is fully dissolved, a blended solution of hydroiodic acid and methylamine (CH_3NH_2) is added to the heated, mixed solution. After the combined solution is mixed, the temperature of the solution is decreased to 75 °C and left for a day until precipitation occurs for small MAPbI_3 single crystals. These small crystals are washed with diethyl ether and dried in vacuum to be used for the next step of large single crystal growth. The leftover solution from the first step is transferred to a new bottle for use in the step for large single crystal growth. The schematic in Figure 1.8 shows the setup for the second step of the TSSG crystal growth technique for acquiring large MAPbI_3 single crystals. During this step, the small crystals grown in step one are placed in the bottom of the leftover solution.

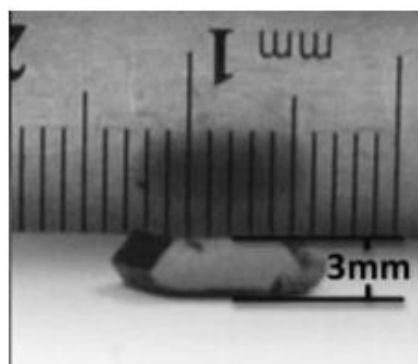
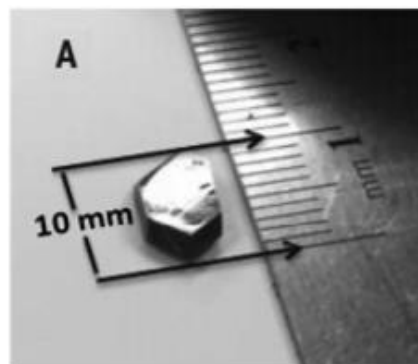
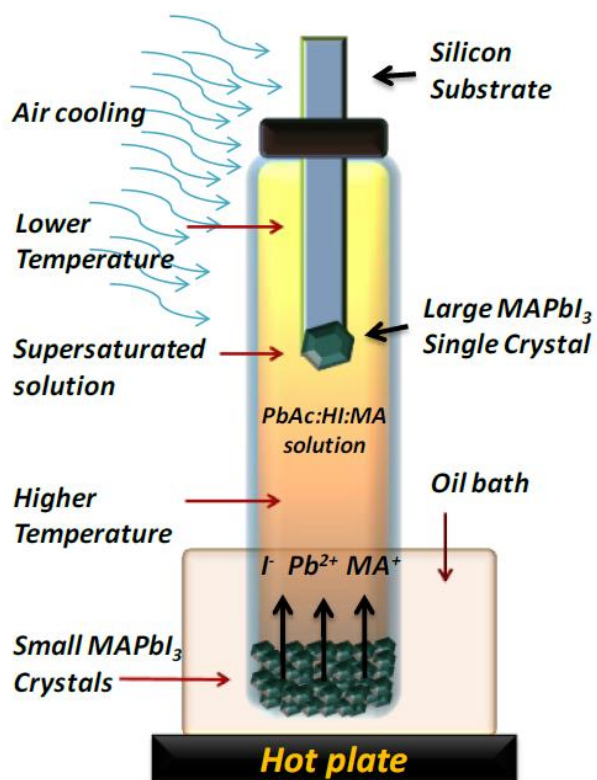


Figure 1.8. (Left) Schematic of top-seeded solution growth for $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. (Right) MAPbI_3 single crystals grown from TSSG method. Reproduced from ref. 46 with permission. Copyright 2015 Science.

A silicon substrate is then inserted from the top of the growth vial. The vial of solution is paced in an oil bath at 75 °C, which acts as a hot-zone for the crystallization. Outside of the vial, the silicon substrate is air-cooled to create a cold-zone on the substrate to facilitate nucleation by removal of latent heat in the system. With this method, large MAPbI₃ single crystals can be grown with good environmental stability, as it has been reported that these crystals can maintain their shiny surface appearance for up to 6 months, as shown in Figure 1.8 (right).⁴⁸ Although this growth technique has shown great success in synthesizing large, high quality, long-term stability MAPbI₃ single crystals, many disadvantages are concerning for the applicability of this technique. As discussed in section 1.3, a main advantage for this material class is the ability of cation/anion substitution to tune band gaps and electronic properties. Because this technique is only used for MAPbI₃, it eliminates the opportunity for simple doping/substitution techniques to modify the chemical composition. Also, the raw materials needed for this crystal growth method are more expensive than materials needed for other solution-based methods to be discussed. Because of this, the TSSG method is not as cost-effective as other methods. Along with the raw materials being more expensive, there is much more material and chemical waste using this method after growth, driving down the yield from this method and again increasing the cost. Figure 1.9 (top) shows a schematic diagram of the AVC method for growing MAPbX₃ single crystals, as shown in Figure 1.9 (bottom). This method is more cost-effective, and simpler than TSSG discussed previously. In the AVC method, a crystallization solution is prepared by mixing precursors of MAX and PbX₂ (X = Br⁻ or I⁻) in the appropriate solvent (either N,N-Dimethylformamide (DMF) or γ -butyrolactone (GBL)).

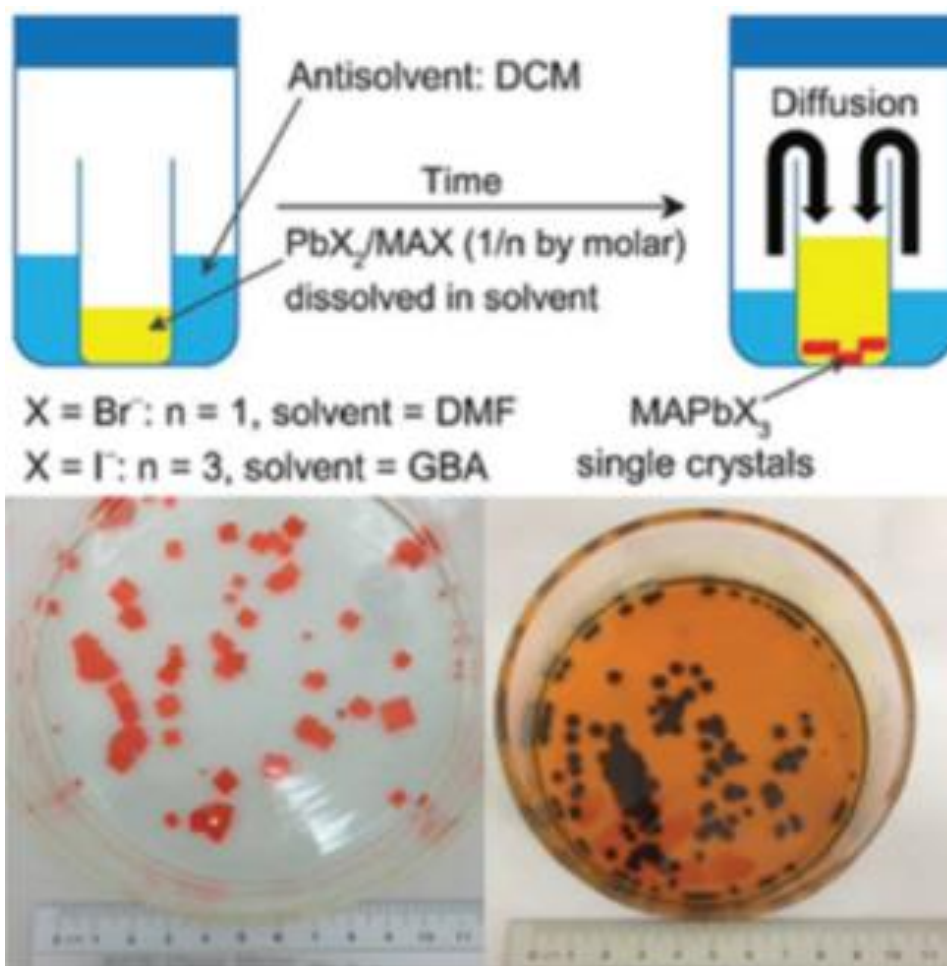


Figure 1.9. (Top) Schematic of AVC single crystal growth method. (Bottom) MAPbBr_3 and MAPbI_3 single crystals grown via the AVC method, from left to right, respectively. Reproduced from ref. 47 with permission. Copyright 2015 Science.

Once the solution is completely dissolved and filtered, the open solution is placed inside of an outside container. The outside container contains an antisolvent, which is dichloromethane (DCM) in the case for these MAPbX_3 compounds. The outside container is then closed off from the outside environment. Once this set-up is complete the antisolvent slowly diffuses into the solution, which causes nucleation and crystallization of small MAPbX_3 single crystals. The crystallization rate can be controlled via size of the opening between the solvent and antisolvent containers or by temperature. This method has been reported to produce high quality, millimeter sized crystals, with a very cost-effective approach.⁴⁹ However, there are still concerning disadvantages to the AVC method. The main disadvantage for this method is that there is little control over the nucleation and crystal growth parameters once the vapor diffusion process begins. Therefore, although this method grows high quality MAPbX_3 single crystals suitable for fundamental studies on electronic properties, the size is too small for fabricated devices for application. Figure 1.10 (top) shows a schematic diagram of the ITC method for growing MAPbX_3 single crystals, as shown in Figure 1.10 (bottom). In the ITC method, an MAX/PbX_2 solution is prepared in the proper solvent ($\text{X} = \text{Br}^-, \text{Cl}^-, \text{I}^-$). Each of these materials has an inverse relationship between solubility and temperature. This means that when temperature increases, solubility of the MAX and PbX_2 precursors decreases.⁵² Once the solution is fully dissolved and filtered, the prepared solution can be split into separate vials and all placed in an oil bath for even heating. Compared to the other solution-based growth methods, the ITC method has shown to be a cost-effective growth method capable

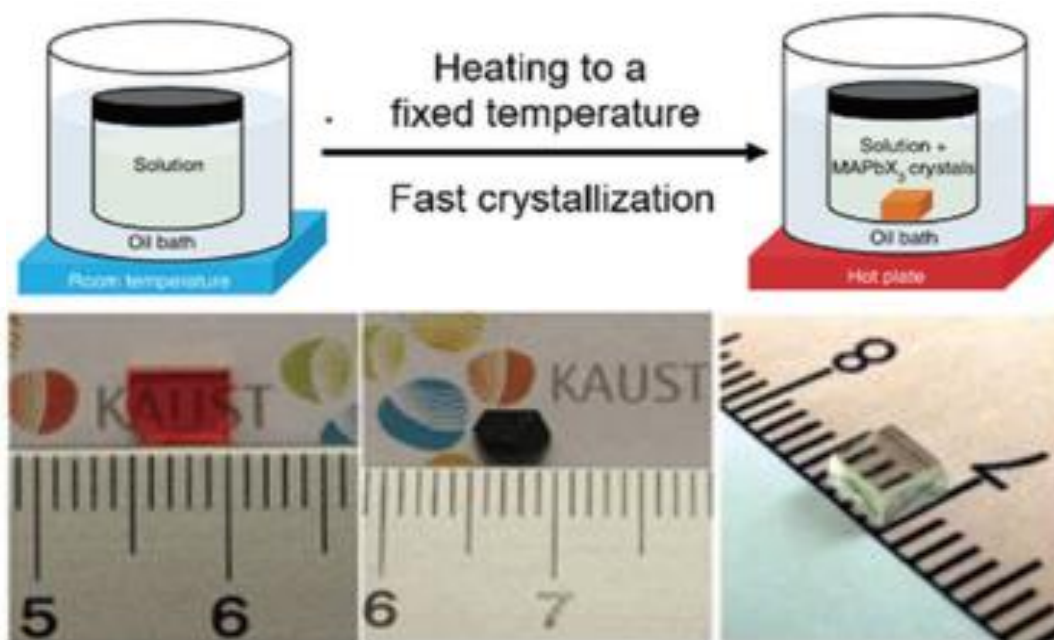


Figure 1.10. (Top) Schematic of inverse temperature crystallization method. Reproduced from ref. 48 with permission. Copyright 2015 Nature Communications. (Bottom) MAPbBr₃, MAPbI₃, and MAPbCl₃ single crystals grown via the ITC method, from left to right, respectively. Reproduced from ref. 49 with permission. Copyright 2015 The Journal of Physical Chemistry Letters.

of producing large volume, high quality single crystals with minimal material waste and accurate control over nucleation and crystallization parameters.⁵⁰⁻⁵¹ Because of the advantages of accurate growth control and the ability to grow large volume, high quality single crystals, this solution-based growth method has been shown to be the optimal growth method for MAPbX₃ single crystals. Also, the ability to modify the composition of the solution, with proper solvent engineering, enables a simple method to dope crystals for multiple cation/anion substitutions. Therefore, the ITC method will be the focus for crystal growth in the following research.

2 Applications of OMHPs

To understand the general properties and mechanisms of OMHPs and OMHP device structures in applications, an introduction on radiation detection including radiation interactions with matter, different types of detectors, and an overview on progression of OMHP semiconductor detectors will be reported in section 2.1. Subsequently, in section 2.2, an overview of other optoelectronic applications will be discussed, as the development of this material is useful in these technologies as well and is important towards understanding of fundamental properties of the material for all applications.

2.1 High Energy Radiation Detection

2.1.1 Radiation Interactions with Matter

High energy radiation exists in many different forms, including alpha particles (heavy charged particles), fast electrons, neutrons, x-rays, and gamma rays. These types of radiation can be distinguished in many ways, including a general category of charged and uncharged radiation particles. First, alpha particles and fast electrons are charged particle radiations, which means that the particle carries a charge with it. Because of this, the radiation can interact via Coulomb force with electrons in any material the radiation passes through. In these cases, charged particles tend to deposit all their energy into the surface of a sensing material with low penetration depth. This makes nuclear reactions inside of a detector with charged particles simpler, with no position dependence. On the other hand, neutrons, x-rays and gamma rays are all known as uncharged radiation, where the particle of radiation carries no net charge, which means they do not interact via Coulomb forces like charged particles. Because of this, these uncharged radiations must undergo an interaction that drastically changes the properties of the incident radiation during an encounter. When an interaction occurs, the incident radiation transfers some to all its

energy to electrons or nuclei of atoms in the sensing material, or into charged particle products of nuclear reactions with materials. If an interaction does not occur between the sensing material and uncharged incident radiation, the radiation particle passes through the material without any detection. Here, the mechanisms of different types of uncharged radiation interactions with matter are discussed in detail.³

Neutrons do not directly ionize atoms, so they are detected indirectly after they produce a charged particle or photon, which can then be recorded by a detector. The charged particle or photon is produced when the neutron interacts with the nucleus of an atom. If the mechanism of the neutron interaction is known, then detailed information can be discerned from the incident fast or thermal neutrons. These neutrons can be detected in many ways including absorptive and scattering reactions. In absorptive reactions, the neutron interaction with the nucleus produces another radiation type, (α , p , γ , or fission) and the neutron is detected via interactions between the sensing material and the produced particle. The scattering reactions is mainly through neutron-proton collision, where the proton knocked out from the neutron interaction is recorded. This is known as the proton-recoil method. Because a neutron and proton have similar mass, a neutron may deposit a range of energy from zero to all its energy to a proton. Then the movement of the displaced proton can be detected.³

Gamma rays and x-rays can also transfer a range from zero to all its maximum energy to ionized electrons within the sensing material. These incident radiation particles can interact with matter in three main ways as described in Figure 2.1.

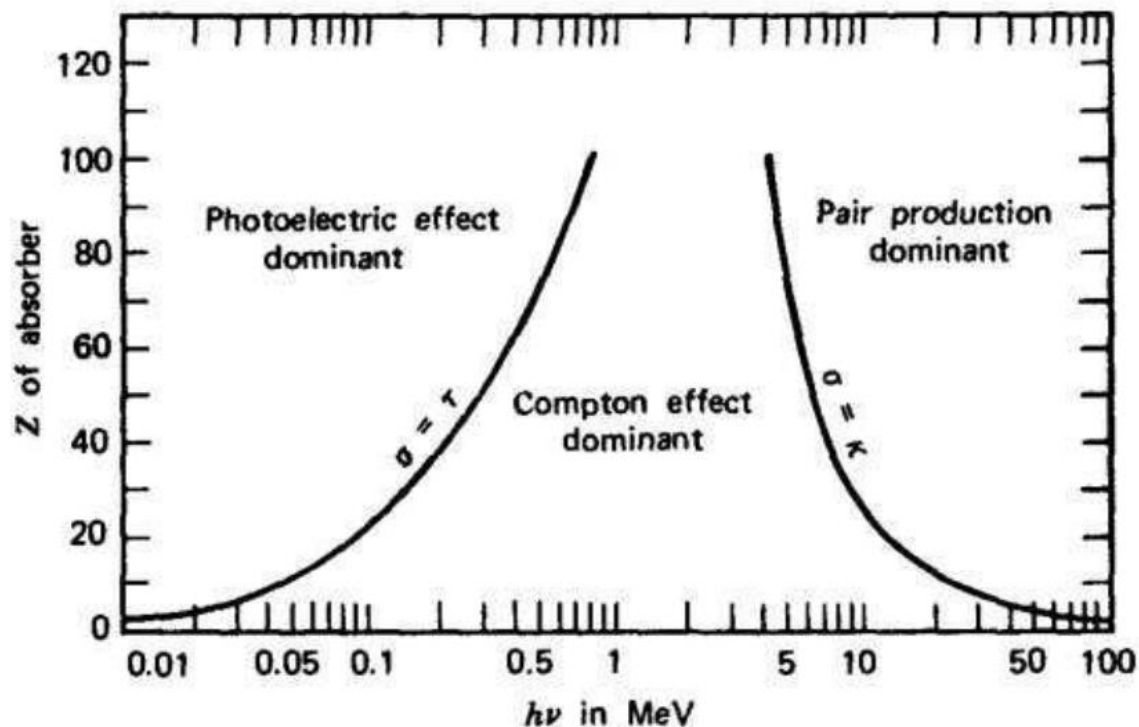


Figure 2.1. Relative importance of three major gamma interactions. The left curve indicates materials of atomic number Z , where photoelectric effect and Compton scattering have equal probabilities to occur. The right curve indicates materials of atomic number Z , where Compton scattering and pair production are equally probable to occur.³

The interactions that take place between these radiation particles and electrons include: photoelectric absorption, Compton scattering, and pair production.³ The occurrence of these three phenomena are shown in Figure 2.1., where the phenomena are plotted as a function of material atomic number and radiation particle energy.

The photoelectric effect occurs when a photon interacts with a bound atomic electron. When this interaction occurs, the photon completely is completely absorbed and a free electron (called a photoelectron) is ejected from one of its bound shells in the atom. Equation 2.1 describes the kinetic energy of the photoelectron, E_{e^-} ,

$$E_{e^-} = E_{\gamma} - B_e \quad (2.1)$$

Where E_{γ} is the energy of the incident gamma photon and B_e is the binding energy of the electron that is ionized. As seen in Figure 2.1., this process is dominant for low energy x-rays and gamma rays and is enhanced in high Z sensing materials.

Compton scattering, which is an inelastic scattering process, is the occurrence of an incident photon colliding with a free electron. This process is shown in Figure 2.2., where a recoil electron is the ionized electron and the scattered photon is leftover energy from the original gamma photon with different direction and energy.

An electron can be considered as a free electron when the binding energy of an electron is significantly lower than the energy of the gamma photon. ($B_e \ll E_{\gamma}$) Because the binding energy of the free electron is so low, the incident gamma photon can ionize the electron, while scattering off with a lower energy to create further interactions in the sensing material or pass through the material.

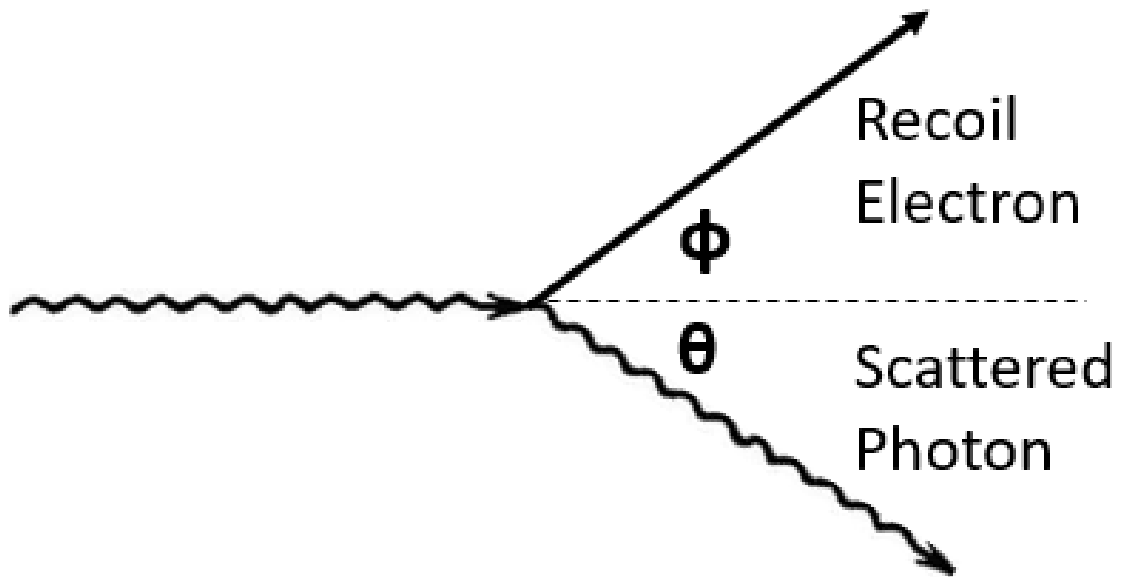


Figure 2.2. Schematic for Compton scattering.

The scattered photon must follow the laws of conservation energy and momentum. Therefore, the energy of the scattered photon can be calculated as a function of the scattering angle θ . This relationship is shown in Equation 2.2.,⁵³

$$E_{\gamma'} = \frac{E_{\gamma}}{1 + (1 - \cos\theta) \frac{E_{\gamma}}{mc^2}} \quad (2.2)$$

where $E_{\gamma'}$ is the energy of the scattered photon, E_{γ} is the energy of the original incident gamma photon, θ is the scattering angle of the scattered photon, and mc^2 is the binding energy of the electron (0.511 MeV). The probability of Compton scattering heavily depends on the number of free electrons available for scattering during an interaction and increases linearly with atomic number Z . As seen in Figure 2.1., Compton scattering is predominant across a wide range of photon energies depending on the absorber material Z .³ Pair production is the final high probability interaction that takes place when gamma-rays interact with matter. In this phenomenon, the interaction takes place between a gamma photon and a nucleus. When this interaction takes place, the photon is fully absorbed, and an electron-positron pair is produced. After this interaction, the nucleus does not undergo any changes. The rest mass of the electron and positron are equal at 511 keV. Therefore, for this interaction to occur, the incident gamma photon must be greater than or equal to 1.022 MeV. If the energy of the gamma photon is greater than the 1.022 MeV threshold, the excess energy from the incident gamma photon is shared equally by the electron and positron as kinetic energy, explained in Equation 2.3.,

$$T_{e^-} = T_{e^+} = \frac{1}{2}(E_{\gamma} - 1.022 \text{ MeV}) \quad (2.3)$$

where T_{e^-} and T_{e^+} are the kinetic energies of the electron and positron from the electron-positron pair, respectively. Because this process requires that the energy of the gamma photon be greater than 1.022 MeV, it is shown in Figure 2.1. that pair production is the predominant interaction mechanism for high energy gamma photons.

2.2.2 Solid State Detectors

Solid state detectors have greatly increased in attention over gas radiation detectors due to much higher densities yielding greater stopping power to incident radiation. Therefore, solid state detectors can be created with much smaller volumes, while still retaining efficient radiation absorber properties.³ There are two functional categories of materials known as semiconductors and scintillators. In both cases high energy radiation particles induce primary interactions via ionization processes, which interact within the volume of the absorber material. This occurs on a picosecond timescale, creating electron-hole pairs (excitons). These electron-hole pairs are then processed into electrical signal in very different ways in semiconductors and scintillators further explained in detail.

Scintillator detectors rely on luminescent properties of the sensing material. When the radiation interaction occurs, electron-hole pairs are generated in the material. These electron-hole pairs undergo radiative recombination, resulting in the emission of photons (typically in the visible wavelength spectrum). The photons emitted from these materials is then captured by an optically coupled photo-multiplier tube (PMT) or photodiode, which converts the emitted photon signal to an electrical signal associated with the energy of the incident radiation source. The fundamental principles of a scintillator coupled with a PMT are shown in Figure 2.3,

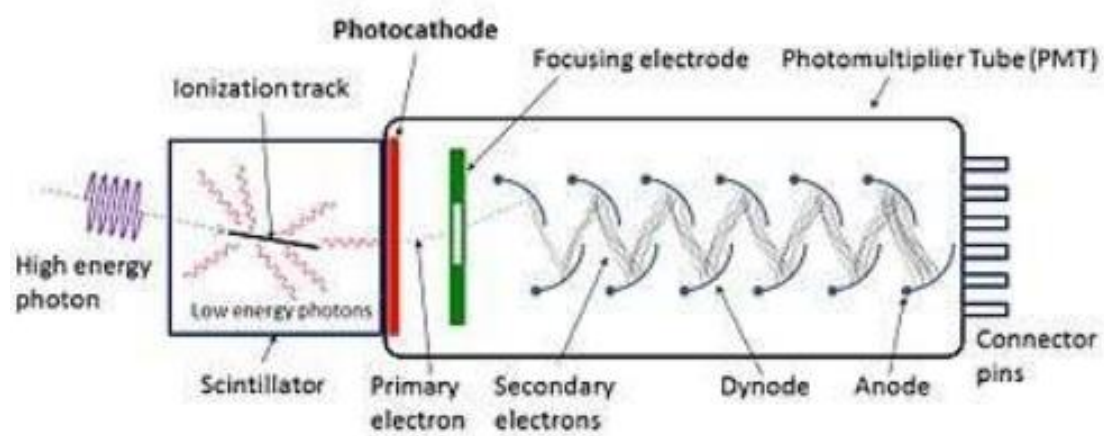


Figure 2.3. Schematic representation of a scintillator coupled with a PMT.

where a low energy photon emitted from the scintillator strikes the photocathode and ejects an electron from the photocathode due to the photoelectric effect. This electron then passes through a focusing electrode and is directed at dynodes inside of the PMT. These dynodes use secondary emissions to multiply the original electron to enhance the weak signal into a proper readout for radiation sensing.⁵³ In this process, recombination of electron-hole pairs is essential for radiative recombination yielding light emission. Therefore, activation centers are often introduced to large bandgap materials to increase radiation probability. This mechanism of radiative recombination is the opposite direction from semiconducting materials, where charge separation is essential.

Semiconducting radiation detectors instead use an applied external electric field across the device to help dissociate electrons and holes to positive and negative electrodes, respectively. This photocurrent is directly recorded as current output of the radiation detection, which is a more direct conversion mechanism compared to scintillators. A schematic diagram of the semiconductor detector is shown in Figure 2.4. Because of this, semiconductors can potentially provide faster response times with better signal-to-noise ratios.

Whichever mechanism is chosen for a solid state detector, the sensing material must have high stopping power to maximize interaction probability coupled with capability of growing large volumes for high interaction volumes, low density of traps to minimize charge trapping, and good uniformity to reduce scattering effects.³

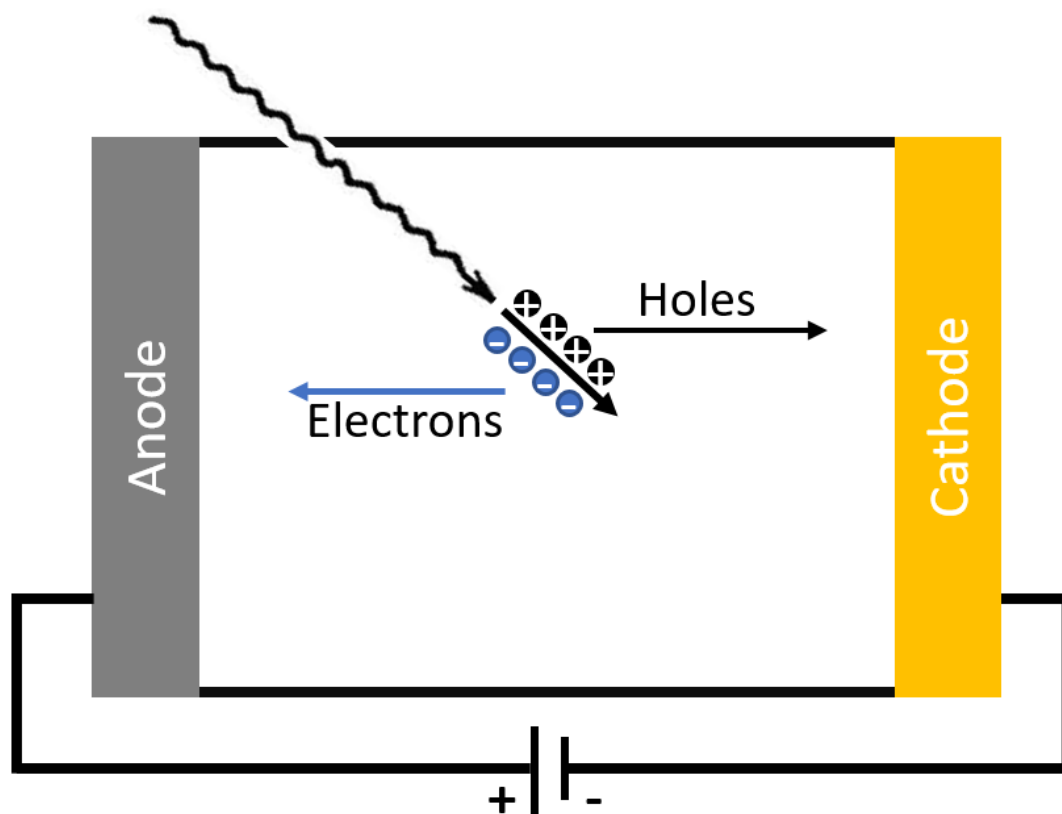


Figure 2.4. Schematic diagram for a semiconductor radiation detector.

In this work, the focus is using MAPbBr₃ single crystals for semiconductor radiation detectors. Therefore, it is important to understand the history of semiconducting radiation sensing materials and requirements to develop a novel semiconductor detector material. A few of the standard materials that have been commercially developed as semiconducting radiation sensors include high purity silicon, HPGe, and CZT. Silicon and HPGe both have extremely high energy resolution; however, they can only perform at cryogenic temperatures due to thermal processes creating too much leakage current. CZT has been developed with good energy resolution at room temperature. But this material is difficult to grow large volumes with high purity ($>1000 \text{ cm}^{-3}$). Because these available technologies have these significant drawbacks, development of novel semiconducting sensing materials is essential for wide-spread development of radiation detection technologies. In order to produce such technology, a novel radiation detection semiconductor must meet certain requirements including: **high radiation sensitivity** to produce a processable electronic signal, **high resistivity** to enhance signal-to-noise ratio, low intrinsic carrier concentration to minimize effects of leakage current, a **band gap** large enough to eliminate leakage current from thermal processes, but small enough to ensure sufficient electron-hole pairs are created via small electron-hole ionization energy, **high atomic number (Z)** and **large interaction volumes** for efficient amounts of radiation interactions inside the material, **high $\mu\tau$ -product** to achieve high charge collection efficiencies via **high, balanced charge mobility (μ)** coupled with **long charge carrier lifetimes (τ)**, **high purity** to reduce scattering effects, and **long material stability** to have sufficient lifetime of a detector. In this research, OMHP single crystals are proposed to be

developed to meet all these critical requirements for an efficient, low-cost semiconductor radiation detector.

2.2.3 Radiation Detection based on OMHPs

Although there have been limited reports of OMHP radiation detectors, the material looks promising in its early stage of development for low-cost, high resolution, room temperature radiation detectors. Pertaining to the requirements mentioned in section 2.2.2, research has shown that properties of OMHP single crystals are sufficient for most of these requirements.

- The tunability of band gap discussed in section 1.3 is desirable as the band gap can be modified to have low leakage current with sufficient electron-hole generation for high signal-to-noise ratios.³⁸⁻³⁹
- Early reports of radiation sensing have shown adequate signal due to high radiation sensitivity.^{20-21, 54}
- Many reports have high resistivities of OMHP single crystals grown for detection on the order of 10^8 - $10^9 \Omega$ for minimal leakage current.²⁰⁻²¹
- OMHPs that have gained attention in radiation sensing are MAPbX₃ structures. The lead component in these materials satisfies the high atomic number needed for high stopping power, and large volumes have been produced, with reports showing up to two-inch crystals grown with simple solution-based techniques.

- High $\mu\tau$ products have been reported up to $10^{-2} \text{ cm}^2/\text{V}$ for different MAPbX₃ compositions, yielding adequate charge collection properties for radiation sensing.²¹⁻

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- Reports have shown that these single crystal devices can be very stable without any obvious external quantum efficiency (EQE) loss after months of storage in ambient conditions in air.²¹
- Long carrier lifetimes associated with low trap densities have been reported on a scale of over 100 μm ,⁴⁸ with reported trap densities as low as 10^6 cm^{-3} .²¹ Even when defect concentration is higher in OMHP single crystals, this material has shown excellent defect tolerance due to polaron formation allowing Coulomb interactions to be screened and traps to be screened in the process.⁵⁵⁻⁵⁶
- The key drawback to OMHP single crystals for radiation sensing is their relatively low charge mobilities as compared to CZT and other standard detection materials. Many reports have calculated hole and electron mobilities $1 < \mu < 100 \text{ cm}^2/\text{V} \cdot \text{s}$ for MAPbX₃ single crystals and have shown that electron mobilities are usually much less than hole mobilities.⁵⁷ Meanwhile, the electron mobility of CZT is experimentally observed at $\sim 1000 \text{ cm}^2/\text{V} \cdot \text{s}$.⁵⁸ To produce high resolution gamma-ray radiations sensors, the charge mobilities of OMHP single crystals needs to be drastically improved. Not only do the electron and hole mobilities need to be significantly increased, but they also need to be properly balanced for sufficient CCE of devices.

This work aims to provide significant experimental insight towards the development of OMHP single crystals towards achieving adequate properties in all of the areas of interest

outlined above to produce a novel room temperature, high resolution, low-cost radiation sensing material.

2.2 Optoelectronic Applications

Although this work focuses on the application for high energy radiation detection, the fundamental understanding and development of OMHP single crystals is also beneficial for a wide range of optoelectronic applications as well. Not only is the work useful for optoelectronic applications, studying these applications can also provide significant insight towards radiation detection, as the fundamental mechanisms of charge transfer and charge collection is similar between optoelectronic applications and radiation sensing. For instance, photodetection and photovoltaic applications require the absorption of visible light photons that generate electron-hole pairs in the absorber material, which are then separated to generate a processable electrical signal for photodetection or electricity in the case of photovoltaics, which is similar to semiconductor-based detectors. On the other hand, LED technology is similar to scintillation-based detectors, where the recombination of electron-hole pairs is required for light emission. Because of the fundamental comparisons between optoelectronic applications and radiation sensing, it is important to understand the basic similarities and differences between these applications to gain a deeper understanding into the development of OMHPs.

Photovoltaics and photodetectors share similar charge transfer mechanisms. The difference is that the incident photons in photovoltaic and photodetector applications comes from low energy (eV range) visible light, whereas incident photons from radiation are much higher energy (keV to MeV range). Considering UV-Visible light, light-matter interactions occur

through absorption of the incident photon, which excites electrons of the material, creating electron-hole pairs. Once the electron-hole pairs are generated the process of charge transfer and charge recombination can be similarly studied between optoelectronic applications and radiation sensing, as seen in Figure 2.4. Single crystal OMHPs are not useful as photovoltaics due to their thickness and high absorption coefficients. This limits the penetration of photons from visible light throughout the bulk of the material, which inhibits the maximum amount of electron-hole pairs able to be generated. Therefore, photodetection can be a useful tool towards understanding charge separation and charge transfer in all applications (schematically shown in Figure 2.5). Literature has shown that tunable band gaps can be useful to synthesize OMHP photodetectors suitable for a wide range of wavelengths.⁵⁹ In a photo detector, light is absorbed by the absorber material (in this case OMHP) and the absorbed photons excite electrons from the VB to the CB, creating electron-hole pairs. These electron-hole pairs are dissociated to their respective electrodes via either a small bias to the device (typically ~ 1 V) or a built-in potential by offsetting the band structure of the device. Photodetection can be used to understand charge transfer properties and response/relaxation times to photoexcitation. Information gathered from photodetection can help develop OMHP electronic properties towards efficient radiation detection. Opposite of charge transfer, understanding charge recombination is an essential fundamental principle towards developing proper scintillation materials and is also helpful

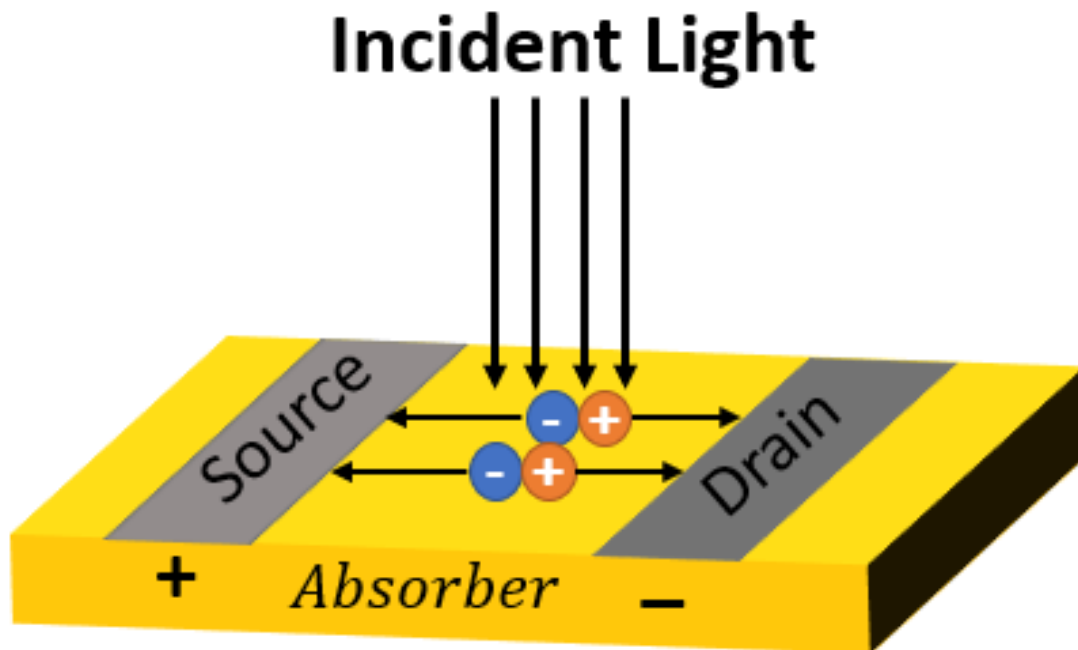


Figure 2.5. Schematic diagram of a photodetector.

to understand in semiconductors, which require reduction of radiative and non-radiative charge recombination. Scintillation is similar to LEDs in charge recombination mechanisms. In both applications, the radiative recombination of charge produces light emission.

In this way, although this work focuses on the development of OMHP single crystals towards radiation detection application, the fundamental physics behind electronic properties of the material are also important for optoelectronic applications. Therefore, this work can provide insight towards radiation detection and other optoelectronic applications, such as photovoltaics, photodetectors and LEDs. Also, these optoelectronic properties can be used as an experimental tool to better understand the electronic properties of the material to help further develop the fundamental understanding and device physics for all applications.

3 Materials and Methods

In this chapter the procedures carried out through the experimental work will be explained. In section 3.1, sample preparation will be discussed in detail including materials and tools used. Then, in section 3.2, the procedure of device fabrication for different device setups will be provided. Section 3.3, will provide details for main experimental measurement schematics and explanations.

3.1 Single Crystal Growth and Materials

All OMHP single crystals studied in this work were synthesized as part of this work. All materials used for OMHP single crystal synthesis were purchased and used as received. Single crystal precursor materials for growth of MAPbBr_3 , MAPbCl_3 , $\text{MAPbBr}_{3-x}\text{Cl}_x$, and FAPbBr_3 single crystals include lead (II) bromide (PbBr_2 , Alfa Aesar, 98+%), lead (II) chloride (PbCl_2 , Sigma Aldrich, 98%), methylammonium bromide (MABr , GreatCellSolar, 99+% / Sigma Aldrich, 98% / Osilla 99.5%), methylammonium chloride (MACl , Sigma Aldrich, 98%), and formamadinium bromide (FABr , Sigma Aldrich, 98%). Solvents used for crystal growth solutions include DMF (Sigma Aldrich, 99.8%, anhydrous) and dimethyl sulfoxide (DMSO, Sigma Aldrich, 99.9%, anhydrous). The antisolvent used for post-growth crystal washing is DCM (Sigma Aldrich, 99.8%, anhydrous).

All single crystals in this work were grown using the inverse temperature crystallization method. In this method, precursor materials were mixed in solutions using 20 mL vials and magnetically stirred using a magnetic stir bar at room temperature, with vials wrapped in aluminum foil to avoid light effects during solution processing. After the solution is fully dissolved, the solution is filtered using a 0.2 μm polytetrafluoroethylene (PTFE) filter. Once filtered, the solution is divided among multiple vials using 2 mL per vial. Then the

vials are placed in a silicone oil bath (Sigma Aldrich, for oil baths (from -50°C to $+200^{\circ}\text{C}$)). The oil bath sits on top of an aluminum top hot plate for even heating, and the solution is gradually heated up to a final crystallization temperature, where crystals around a volume of 50 mm^3 are grown over the course of 3 to 5 days. The picture in Figure 3.1 shows the growth process inside of an oil bath for MAPbBr_3 single crystals. Once the crystals completed full growth, the crystals were carefully removed from the vials, excess solvent (DMF or DMSO) was gently dried off using Contec AmplitudeTM ProZorb paper, and then washed with DCM to remove all excess solvent from the crystals. After the crystals were washed and dried, they are stored in a desiccator under vacuum for later use to avoid any environmental effects from ambient air conditions, and the desiccator was covered to avoid any adverse effects from prolonged exposure to light during storage. Crystals were separated and stored in Gel-Pak membrane boxes to protect the soft, brittle crystals from moving during storage to avoid chipping and cracking, as seen in Figure 3.2. More detailed information on experimental growth conditions towards developing the quality of OMHP single crystals will be discussed in section 4.2.



Figure 3.1. Picture showing the growth process via inverse temperature crystallization.

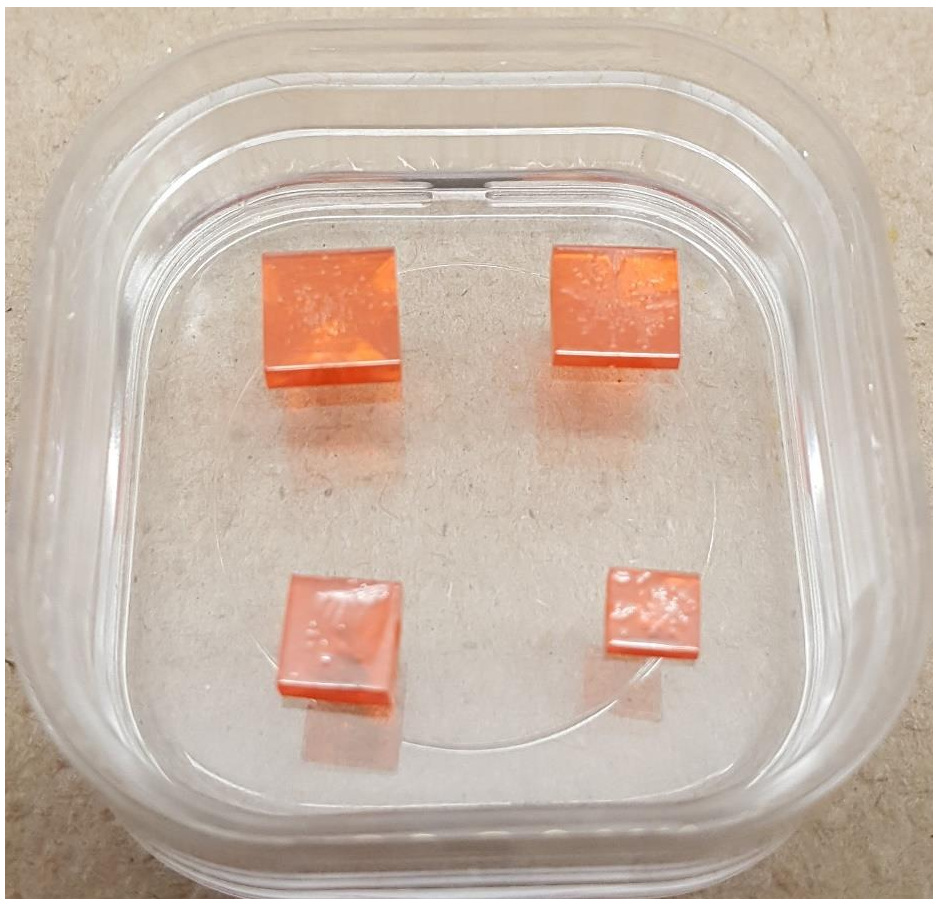


Figure 3.2. Picture of Gel-Pak membrane box used for storage of OMHP single crystals.

3.2 Device Fabrication

For device fabrication all electrode and interfacial materials were purchased and used as received. The evaporation materials include chromium (Kurt J. Lesker, 99.9% pure Cr, Cr-plated tungsten rods), gold (Kurt J. Lesker, 99.99%, 1 mm diameter wire), silver (Sigma Aldrich, 99.99%, shot), (6,6)-phenyl C₆₁ butyric acid methyl ester (C₆₀) (Sigma Aldrich, 99.5%), bathocuproine (BCP) (Sigma Aldrich, 96%). All electrodes and interfacial layers in this work were deposited via thermal evaporation. A schematic showing the thermal evaporation process is shown in Figure 3.3. In the process of thermal evaporation, a source material is placed in a thermal filament, which is connected to a high voltage source. The high voltage source is gradually increased until the deposition monitor begins to read the desired deposition rate. (The source shutter can be used to cover the source to pre-burn any residues off of the source material.) The deposition monitor is calibrated per material using density and acoustic impedance of the source material to be evaporated. Once the desired thickness is reached, the source shutter is covers the source material and the high voltage is gradually decreased until it is off. The system is then allowed time to cool and during this time the evaporated material settles on the substrate. Thermal evaporation is completed at high vacuum levels, typically $<10^{-7}$ torr. Thermal evaporation is commonly used as a physical vapor deposition for deposition of metal and nonmetal materials. Advantages to this method of deposition include deposition of high purity films (dependent on purity of source), the source material can be a solid of any shape or form, the use of shadow masks

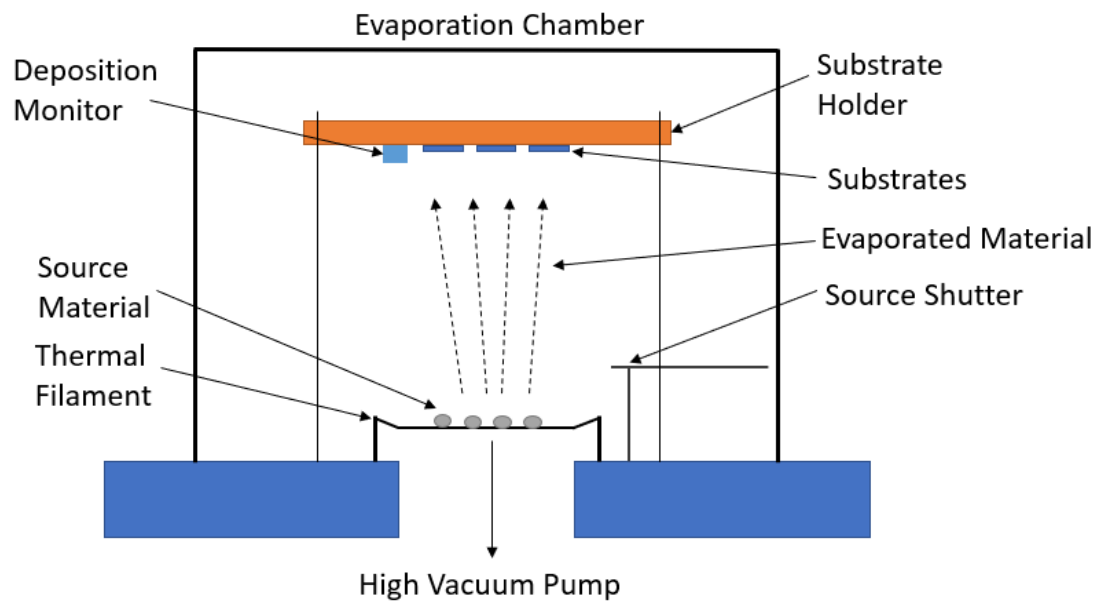


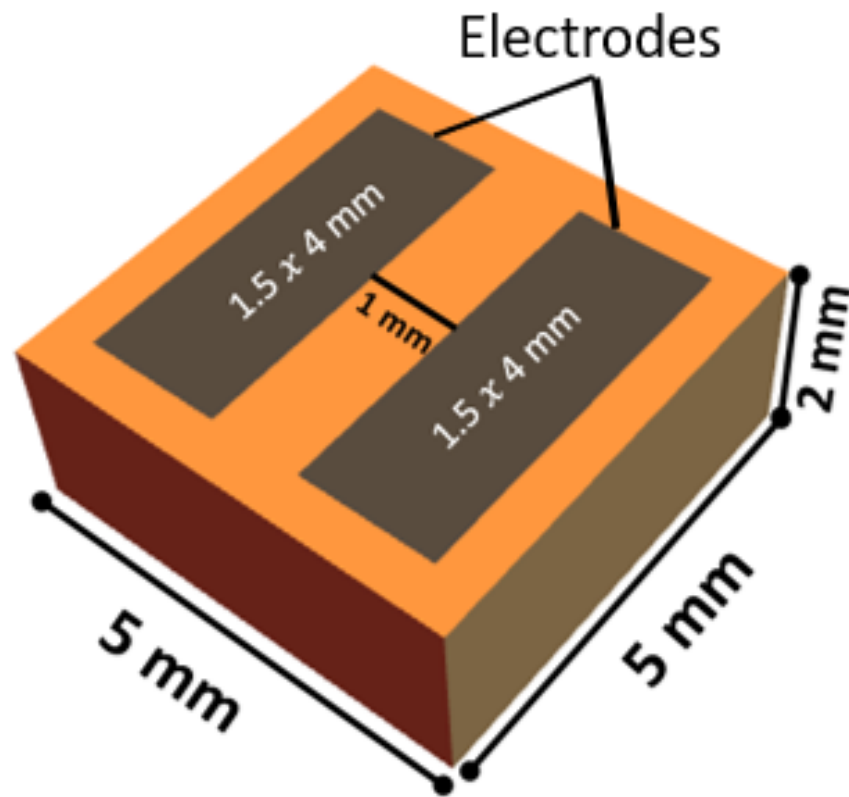
Figure 3.3. Schematic diagram of thermal evaporation system.

allows for deposition of electrodes in specific shapes and sizes, and this option is much cheaper than other PVD or CVD methods and provides simplicity to deposit thin or thick films.

Device fabrication discussed in this section will focus on two different device structures used for experimental work: in-plane and out-of-plane device structure. The in-plane device structure is used for measurements that specifically aim to understand interfacial interactions at the metal/semiconductor interface, as well as photodetection measurements. A schematic is shown in Figure 3.4 for the in-plane device structure.

Out-of-plane devices structures are used when designing devices for radiation detection measurements. This device structure is chosen to acquire a constant electric field through the bulk of the device. A schematic representing the device structure used for radiation sensing devices is shown in Figure 3.5.

The out-of-plane device structure shown in Figure 3.5 is designed when a constant electric field needs to be produced through the bulk of the material. This is required when fabricating devices for radiation detection for proper charge transfer through the device. This device architecture can also be used to measure intrinsic electronic properties of the material when a constant electric field between electrodes is needed, such as mobility measurements. Using the out-of-plane device architecture, interfacial layers can also be implemented to improve charge transfer or prevent specific charge transfer from occurring. Interfacial layers used for this purpose will be discussed in Chapter 5.



OMHP Single Crystal

Figure 3.4. Schematic of in-plane crystal structure for OMHP single crystal devices.

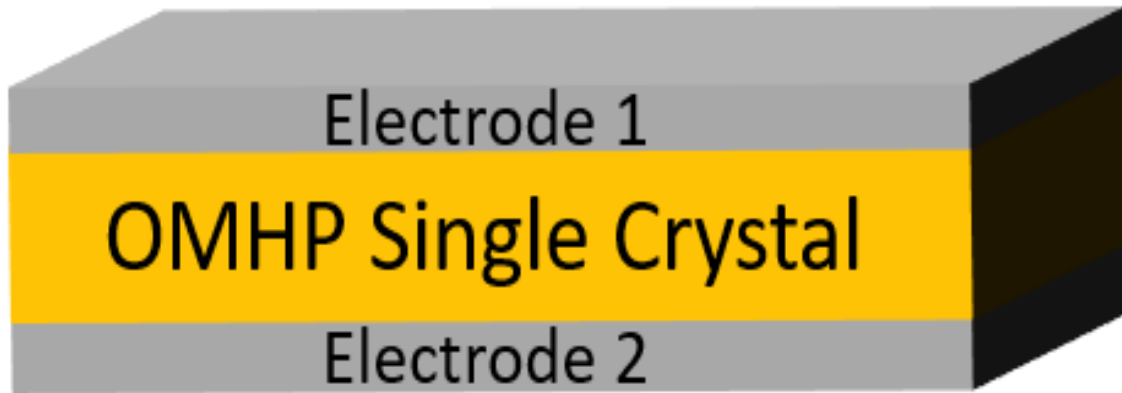


Figure 3.5. Schematic of out-of-plane device structure for OMHP single crystal devices.

3.3 Measurements Setups and Procedures

3.3.1. *Optical Characterization Techniques*

Optical characterization for OMHP single crystals used techniques including UV-vis absorption, steady-state PL, and time resolved photoluminescence. UV-visible absorption is used to determine what wavelengths of light are absorbed or transmitted through a sample material. This method can test for wavelengths in the range of UV light (~200-380 nm) to visible light (~380-800 nm). Sometimes equipment is able to have the capability to test wavelengths in the infrared range wavelengths (up to ~1000 nm). A schematic diagram showing how absorption is measured is shown in Figure 3.6. During the UV-vis absorption measurement, a monochromator (consisting of a white source light, dispersion device and light separating slit) emits wavelengths of light ranging from UV wavelengths to visible wavelengths of light onto the sample. Once the detector is exposed to the light of a certain wavelength, a detector on the other end detects how much light compared to the initial emission intensity is detected after passing through the sample. If the light passes through the sample without any decrease in intensity, there is no absorption of that wavelength. However, if the sample decreases the passing light intensity, the detector measures the new intensity of light and calculates the amount of light absorbed per wavelength. This measurement helps calculate optical properties of materials such as the band edges, which are used to calculate the band gap of a material. If the light passes through the sample without any decrease in intensity, there is no absorption of that wavelength. However, if the sample decreases the passing light intensity, the detector measures the new intensity of light and calculates the amount of light absorbed

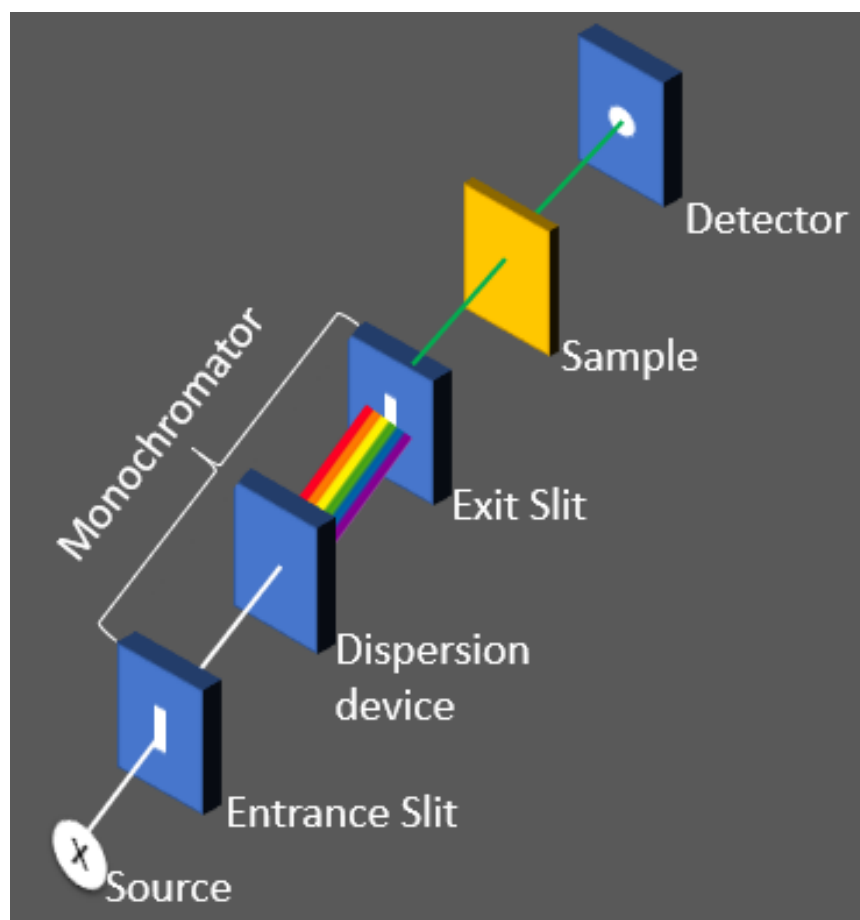


Figure 3.6. Schematic representing a UV-Vis absorption spectrometer.

per wavelength. This measurement helps calculate optical properties of materials such as the band edges, which are used to calculate the band gap of a material.

Steady-state PL and time resolved PL are two similar techniques used to further understand optical properties of materials. PL is the emission of light from any material after absorption of photons from photoexcitation. The process of PL was previously discussed and represented in Figure 1.2. A schematic demonstrating a PL equipment setup is shown in Figure 3.7. In the PL measurement, a laser or LED is used for photoexcitation, which can be passed through optical grating to focus the excitation spot size. Once the photoexcitation is absorbed by the sample, photoluminescence occurs, passes through a photomultiplier tube and is collected using a monochromator. For steady-state PL, a spectrum is collected to find the PL peak position. This PL peak can be compared with the UV-vis absorption edge to better understand the band gap as well as discern information about sub-band gap defects. Similar to steady-state PL, TRPL can be used to discern more specific information about recombination mechanisms of a material. Since PL generates from the recombination of electron-hole pairs, the lifetime of PL can extract important information about the time it takes for radiative recombination to occur. To do this, rather than exciting the sample with a continuous photoexcitation source, a pulsed light source (nanoLED or pulse laser) is used. As the sample is probed by the pulse source, the PL exponentially decays, which can be fit with parameters to understand the lifetime of charge carriers using a simple exponential decay curve.

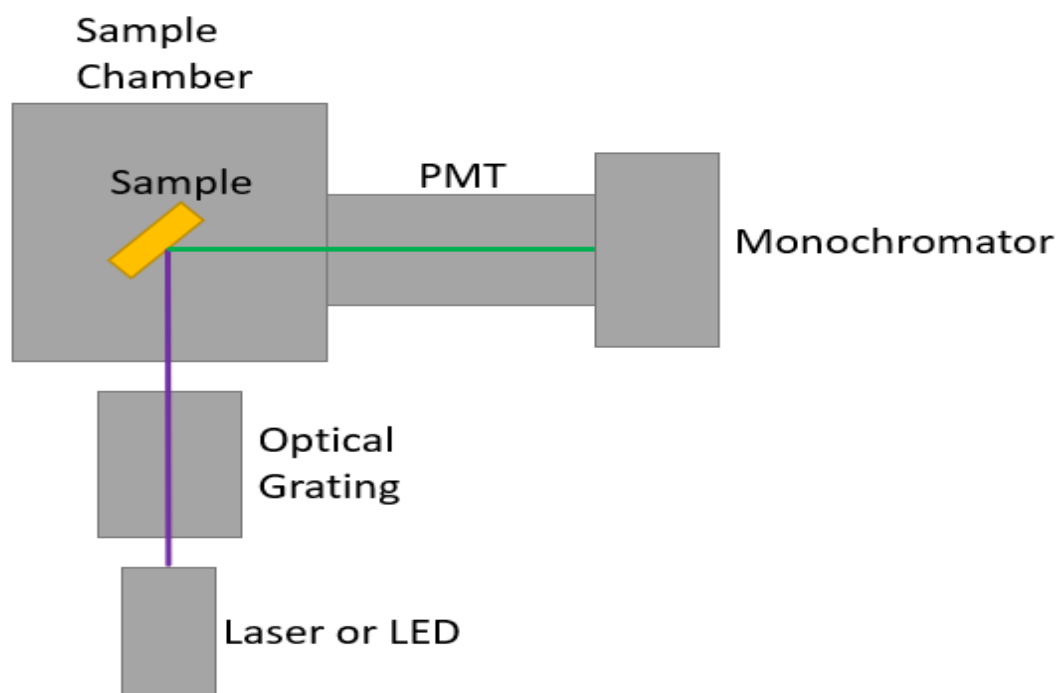


Figure 3.7. Schematic of PL and TRPL equipment.

3.3.2. Electronic Characterization Techniques

Electronic characterization techniques used for OMHP single crystals includes current-voltage (IV) characteristics, space-charge-limited current theory (SCLC), Van der Pauw resistivity, Hall mobility, and impedance spectroscopy. IV characteristics can reveal a great number of important properties about a material intrinsically, as well as about device structures and interfaces depending on the measurement setup. Many IV techniques are used in this work and will be explained in detail when needed for discussion about experimental results. One specific IV technique used for characterizing the electronic properties includes SCLC theory. In this measurement, a curve is generated via current density as a function of voltage or electric field across an out-of-plane device structure. A sample curve generated by this measurement is shown in Figure 3.8. For the SCLC theory to be used for any given material, it is essential that all of the proper curve sections are clearly defined. These sections include the Ohmic region ($I \propto V$), the V_{TFL} region ($I \propto V^3$), and the trap-free SCLC region ($I \propto V^2$). Once these regions have been clearly identified, specific values from the curve can be used along with SCLC equations to estimate intrinsic properties of the material. Equation 3.1 is used to calculate trap density of a material,

$$V_{TFL} = \frac{(e * n_{trap} * L^2)}{2 * \epsilon * \epsilon_0} \quad (3.1)$$

where V_{TFL} is voltage value corresponding to the trap-filled limit, e is electronic charge in Coulombs, n_{trap} is the trap density of the material, L is the thickness of the sample, ϵ is the dielectric constant of the material and ϵ_0 is the permittivity of free space. This equation is then solved for n_{trap} to estimate the density of traps.

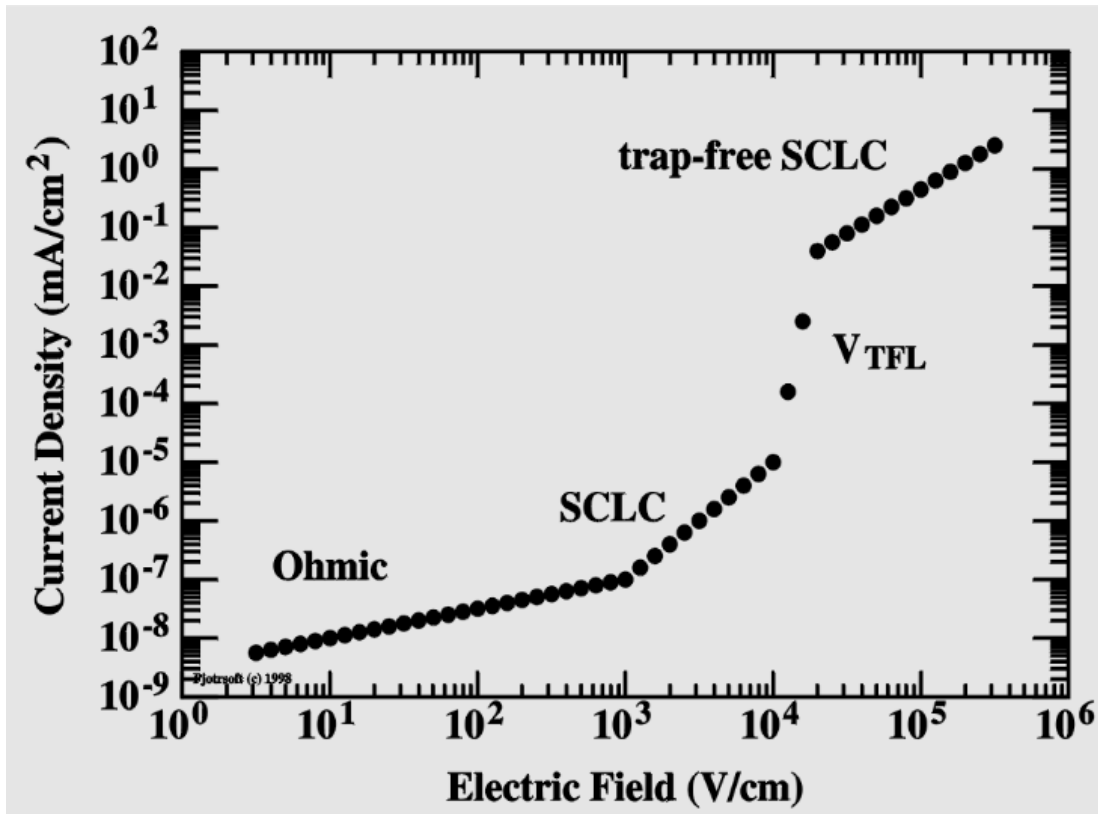


Figure 3.8. Example curve for SCLC model to fit electronic parameters.

Additionally, Equation 3.2 can be used to estimate the charge mobility of a material with SCLC theory,

$$\text{Log}(J) = \text{Log}\left(\frac{q}{8}\right) + \text{Log}(\epsilon_0) + \text{Log}(\epsilon) + \text{Log}(\mu) - 3 * \text{Log}(L) + 2 * \text{Log}(V) \quad (3.2)$$

where J is the current density, μ is the mobility and V is voltage. This equation is then rearranged and solved for μ to estimate the mobility. This characterization method must be used with caution, as the values tend to be highly overestimated compared to other techniques for estimating mobility and trap density. However, the method can be a useful tool to compare similar samples.

Van der Pauw resistivity and Hall effect measurements are another useful tool in estimating intrinsic electronic properties of semiconductors including bulk resistivity and Hall mobility. Figure 3.9a shows a schematic of the Van der Pauw 4-point probe experimental design, and Figure 3.9b shows a schematic of the 4-point probe Hall Effect design. The Van der Pauw resistivity measurement uses a four-point probe technique shown in Figure 3.9a. Electrical contacts are made on four corners of a square-like sample (this technique is beneficial since electrodes do not need to be deposited on the sample). In the schematic, these four electrical contact points are labeled A-D. During the measurement, voltage is supplied to the sample through contacts A to D and current is measured through contacts C to B. Eight configurations are measured in this way, where voltage is sourced across one edge of the sample and current is measured on the opposite side of the sample in the opposite direction of the voltage. Then, directional resistance is calculated for each of the eight configurations via Ohm's Law, which states that $R = V/I$.

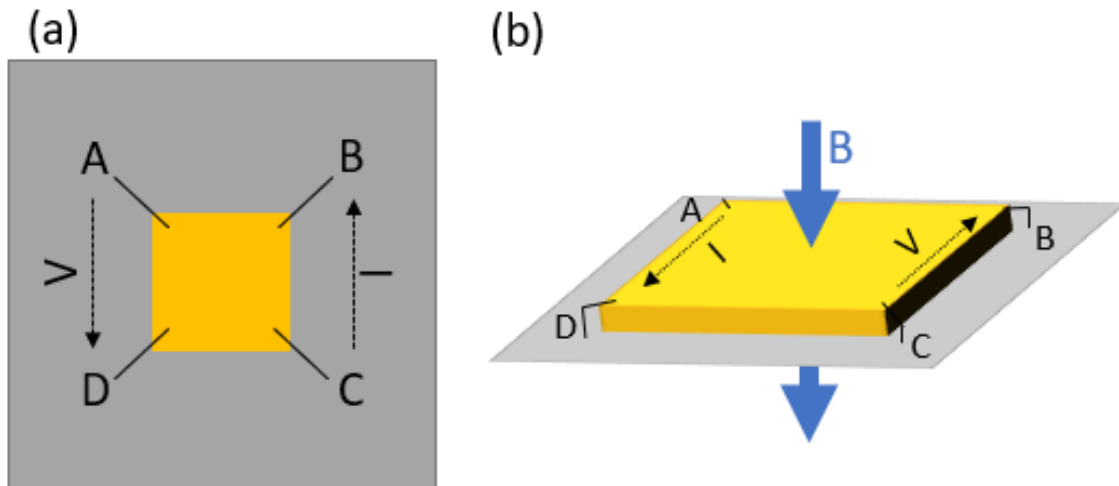


Figure 3.9. Schematic representation of experimental design for 4-point probe (a) Van der Pauw resistivity and (b) Hall Effect using the Van der Pauw technique.

Once the configurational resistances are calculated, the horizontal and vertical resistances are calculated via Equation 3.3 and Equation 3.4, respectively.

$$R_{horizontal} = \frac{R_{BC,DA} + R_{DA,BC} + R_{CB,AD} + R_{AD,CB}}{4} \quad (3.3)$$

$$R_{vertical} = \frac{R_{AB,CD} + R_{CD,AB} + R_{BA,DC} + R_{DC,BA}}{4} \quad (3.4)$$

With values for $R_{horizontal}$ and $R_{vertical}$, (percent error between these values should be less than 5%) sheet resistance, R_s , can be calculated under the condition proposed in Equation 3.5.

$$e^{(-\pi*(R_{horizontal}/R_s))} + e^{(-\pi*(R_{vertical}/R_s))} = 1 \quad (3.5)$$

Multiplying the sheet resistance by the thickness of the sample can then give an estimation for the bulk resistivity of the sample. After the Van der Pauw R_s is solved for, a magnetic field is applied perpendicular to the Van der Pauw measurement, to estimate the Hall voltage, V_H , and Hall mobility, μ_H . The Hall voltage defined in Equation 3.6,

$$V_H = \frac{IB}{qn_s} \quad (3.6)$$

where I is an applied external current, B is the applied magnetic field, q is the charge of an electron and n_s is the majority charge carrier sheet density. To use the Van der Pauw technique to solve for V_H , a magnetic field is applied perpendicular to the Van der Pauw set up as shown in Figure 3.9b. The same configurational measurements are made, except this time current is sourced on one edge in one direction and the voltage is measured on the opposite side in the opposite direction. These measurements are made in four

configurations with the magnetic field oriented in the positive z-direction and again with the magnetic field oriented in the negative z-direction. Then the four voltage measurements are calculated by subtracting the negative voltages from the positive voltages. Finally, the Hall voltage is calculated via Equation 3.7.

$$V_H = \frac{V_{AC} + V_{BD} + V_{CA} + V_{DB}}{8} \quad (3.7)$$

If the Hall voltage is a positive value, the material is p-type (holes are majority carries). If the Hall voltage is a negative value, the material is n-type (electrons are majority carriers). Knowing the Hall voltage, sheet resistance, and majority carrier sheet density, the Hall mobility can finally be calculated using Equation 3.8.

$$\mu_H = \frac{1}{qn_s R_s} \quad (3.8)$$

This method for calculating mobility and other intrinsic electronic properties of semiconductors has shown to be useful in recent literature, as the value is truer to the nature of hybrid perovskites.⁵⁷ Lastly, impedance spectroscopy can be used in many different ways to understand different intrinsic properties of materials as well as interfacial interactions between materials. This measurement will be discussed in more detail when impedance spectroscopy measurements are shown in results for interfacial interactions.

3.3.3. Structural Characterization Techniques

Structural characterization techniques used for OMHP single crystals includes x-ray diffraction (XRD), optical profilometry, optical microscopy, scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), time-of-flight secondary ion mass

spectrometry (ToF-SIMS), and Raman spectroscopy. XRD and powder XRD can be used to characterize crystal structure of a material. In XRD, incoming x-rays of a known wavelength interact with the material of interest. The material has a defined crystal structure with a spacing between scattering atoms, d . When the x-rays interact with the scattering electrons, secondary emission is generated from the electrons, which is known as elastic scattering. The diffracted pattern is measured with intensity as a function of the diffraction angle, θ , and is recorded as a diffraction pattern. These waves will only add constructively when Bragg's Law applies, which is schematically shown in Figure 3.10 and described by Equation 3.9, where λ is the wavelength of the incident x-ray.

$$2 * d * \sin\theta = n\lambda \quad (3.9)$$

Each constructive wave emitted from the scattering electrons in the material will form an x-ray diffraction pattern, which is useful to determine crystal structure and phase of a material and can also be used to help understand disorder and crystallinity in samples.⁶⁰ To directly measure the mosaicity and alignment of crystalline samples, (derived from measurement of epitaxial thin films) high-resolution XRD can be used with a technique known as a triple-axis rocking curve coupling 2θ and ω scan. θ is the angle between the incident beam and the sample, while ω is the angle of the sample rotation. This technique is schematically shown in Figure 3.11. The triple-axis rocking curve is generated by rotating the sample by a small degree (the ω -axis) while the 2θ scan also rotates. Using a crystal or slit, a single diffraction peak is directly monitored during the measurement by constraining the detector so that only one peak is observed throughout the measurement. This allows a lot of information to be derived from this measurement.

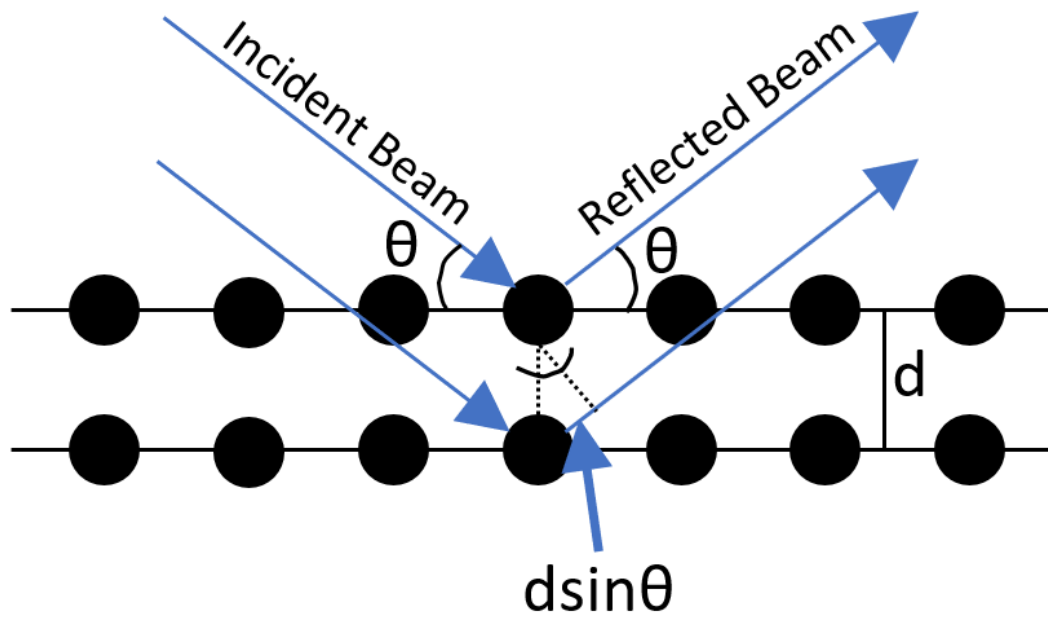


Figure 3.10. Schematic representation of Bragg's Law for x-ray diffraction.

The broadness and symmetry of the peak reveal plane tilt and defect information for the layers of the sample. Broader peaks are attributed to disorder and defects in the sample and mismatch of d-spacing (shown in Figure 3.10). When a triple-axis rocking curve is symmetric, there is no plane tilting throughout the sample, showing that the d-spacing is constant throughout the sample, attributing to high crystalline quality. On the other hand, asymmetry of the triple-axis rocking curve, such as emergence of smaller peaks on either side of the main peak, can be attributed to plane tilting and poor mosaicity (alignment of crystalline domains) of the sample. Optical microscopy and optical profilometry are two imaging techniques used to inspect the surface of material. An optical microscope uses light and a system of lenses to magnify an object to image micron-scale objects of interest such as grain boundaries or crystal inclusions. This can be a useful technique to compare quality of samples through inclusions and/or microcracks in single crystalline samples. Another method of using light for imaging is known as optical profilometry. One common tool used for optical profilometry is white light interferometry. This technique is a simple technique that exposes the surface of a material to white light and measures the reflections from the surface. This technique is commonly used to map surface roughness of a sample. SEM is a microscopy technique that uses a focused beam of electrons to interact with the atoms of the sample material. The atoms emit secondary electrons from the interaction with the incident beam, which are then recorded to give intricate information regarding the surface topography and composition of the sample. This technique for imaging is more detailed than optical methods of microscopy for topography of a material.

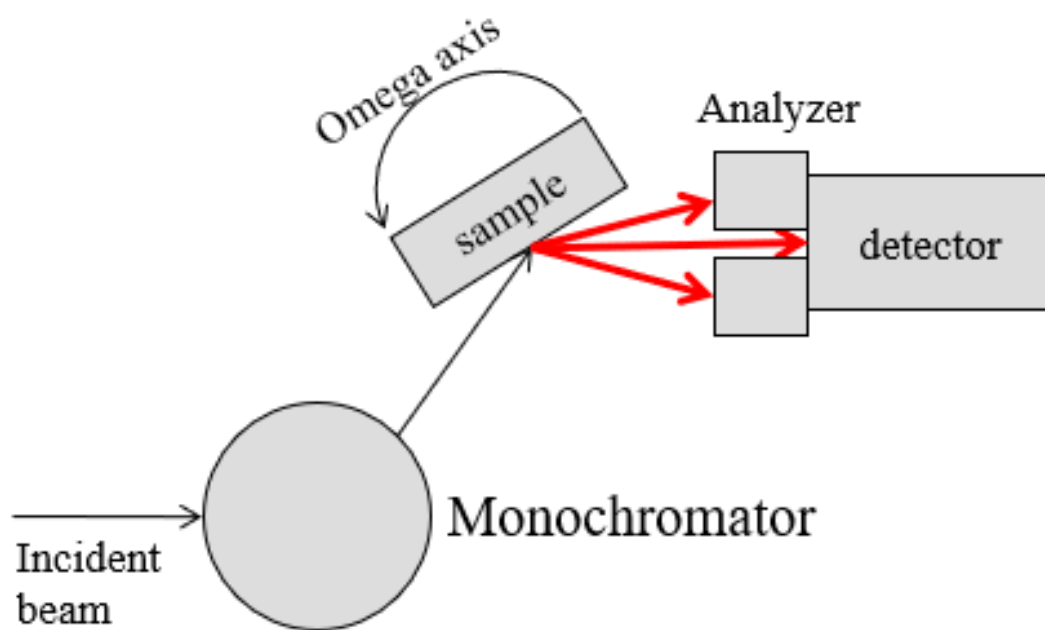


Figure 3.11. Schematic representation of a triple rocking curve.

SEM can also give various amounts of information that optical microscopy cannot. Figure 3.12 provides a schematic of all the various types of scattered electrons and x-rays from SEM imaging. All of these scattered electrons and x-rays refer to very detailed information. Auger electrons can discern atomic composition at the surface. Secondary electrons give topographical information from the surface of the material (SEM). Inelastic scattering of electrons gives detailed information regarding composition and bond states, known as electron energy loss spectroscopy (EELS). Characteristic X-rays give information based on atomic composition of the bulk of the material (EDS). Continuum X-rays come from Bremsstrahlung radiation. Deep in the material, fluorescent X-rays give rise to cathodoluminescence. For the sake of the work completed, SEM and EDS are the tools used to gain a deeper understanding of the OMHP single crystals developed. ToF-SIMS is similar to EDS, except instead of using a focused electron beam to collect secondary emitted electrons from atoms, ToF-SIMS uses a focused primary ion beam and analyzes the emitted secondary ions. Although the techniques are similar, the probe types can yield different types of information. For instance, EDS can accurately calculate type and concentration of high atomic number elements. However, EDS fails when it comes to low Z organic atoms. Meanwhile, ToF-SIMS excels at being able to accurately measure the types and amounts of low-Z elements such as hydrogen or carbon. Therefore, using these techniques together can be useful for determining precise compositions of materials. Finally, Raman spectroscopy is also used in this work to probe differences in local environments for organic cationic motions.

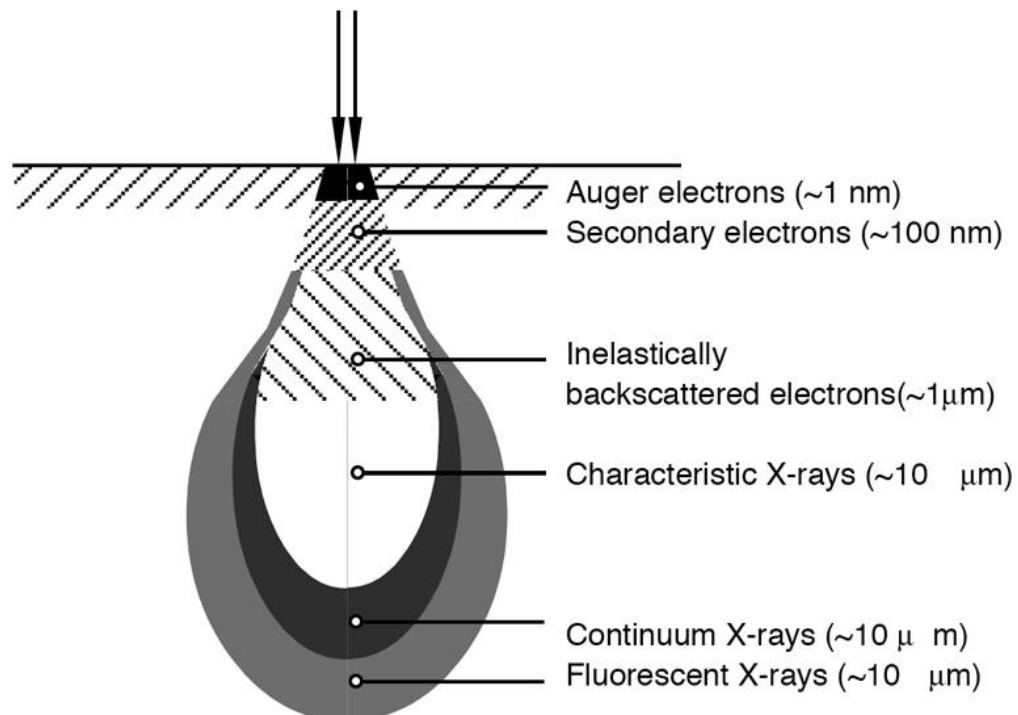


Figure 3.12. Schematic diagram for scattering electrons and x-rays along with interaction volumes from SEM imaging.

In this method, inelastic scattering of monochromatic light from a laser causes shifts in the energy of the photons from the lasers. These shifts identify information about vibrational modes in the material.

4 Synthesis and Characterization of OMHP Single Crystals

In this chapter, results on the growth and characterization of OMHP single crystals will be reported. In section 4.1, more specific information on the effects of growth conditions and optimization will be reported. In section 4.2, results on ion substitution for different chemical composition of OMHP single crystals will be presented. The single crystals focused for this project were MAPbBr₃ single crystals. Therefore, presentation of results will focus on MAPbBr₃ crystals.

4.1 Effects of Growth Conditions

4.1.1. Equipment used for ITC Crystal Growth

As mentioned in section 3.1, all single crystals studied for characterization and device fabrication were grown using the inverse temperature crystallization method, which has been shown to produce large volume, high quality single crystals in a short time frame of hours to days.⁵⁰ When crystals were first being synthesized, the AVC growth technique was also investigated. However, through many attempts the AVC method proved insufficient to grow crystals that had large enough volume suitable for proper device fabrication. Because of this, the AVC method was not heavily investigated, as the ITC method proved to be the most successful and efficient growth method for the requirements of the project. The first important experimental work discussed focuses on the growth of crystals and optimization of the growth technique. Through this optimization, many parameters were deeply investigated. These parameters include the system used for growth,

(inclusion of oil bath, type of hot plate, type and size of vials, amount of solution per vial) temperature paths, precursor ratios, and precursor purities.

To optimize the growth of larger volume, high quality single crystals, the first parameter investigated was the equipment used for growth. At first, ceramic-top hot plates were used without the use of an oil bath. A picture of this setup is shown in Figure 4.1. and pictures of the crystals grown are shown in Figure 4.2. In this setup, the growth of single crystals was successful as shown in Figure 4.1. Pictures of the crystals grown from this method are shown in Figure 4.2. Although, the growth of single crystals was successful using the equipment, it is observed in the pictures of Figure 4.2, that the crystals did not form with a smooth overall shape as seen by the crystals having curved edges and faces. Not only were the crystals grown of poor quality, the growth of crystals without the oil bath and on the ceramic hot plate was inconsistent due to uneven heating of the ceramic-top hot plate. To properly characterize the uneven heating of the ceramic-top hot plate, an infrared thermometer. The ceramic-top hot plate was set at a temperature of 80 °C and left to heat up and stabilize for one hour. Once the hot plate was heated up, the surface of the hot plate was measured with the infrared thermometer in one-square-inch sections to inspect hot or cold spots in the hot plate surface. A heat map is shown in Figure 4.2. It was observed that the closest measurement to the set point of the hot plate was 78 °C, and this temperature was only measured in two of the square-inch measurements. Out of 49 measurements completed on the surface of the hot plate, only ten of these areas measured temperatures between 75-80 °C. All other measurements of the hot plate surface were 10 °C or more below the set temperature.

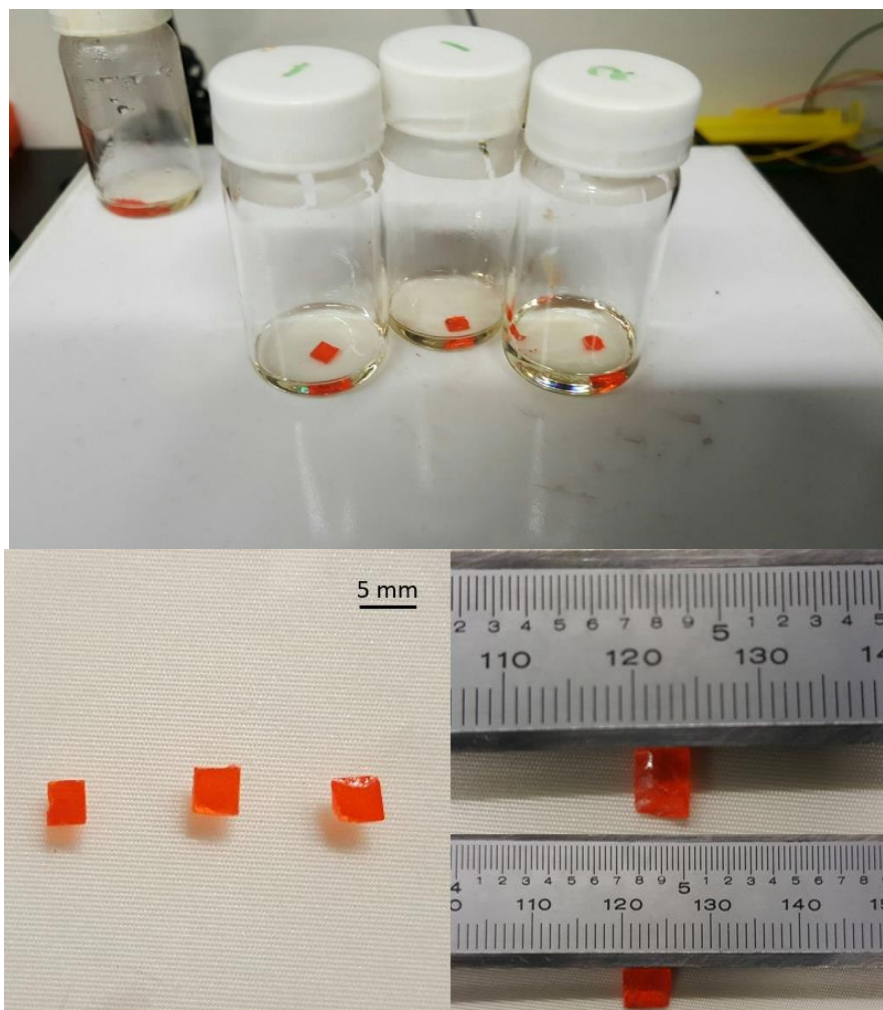


Figure 4.1. Growth of MAPbBr_3 on ceramic-top hot plate in 20-mL vials with different amount of precursor solution pictures of crystals grown from using ceramic-top hot plate.

Because of this, it became clear that the ceramic-top hot plate without the use of an oil bath was insufficient for consistent growth of high quality single crystals. Once this was determined, the equipment used was changed to aluminum-top hot plates for even heating throughout the surface, as well as using an oil bath for additional consistency of heating to the individual vials, as shown in Figure 3.1. Switching to this equipment yielded more consistent growths, producing crystals with sharp corners and edges as well as smooth, flat faces. It was also noted that the amount of solution placed in a vial played a large role in how the crystals grew. Inside the 20 mL vials, when only one mL of solution was used the top surface of the crystal tended to grow out of the solution resulting in a curved face, undesirable for electrode depositions. Therefore, the use of two mL per vial is essential to ensure the crystal is completely submerged in solution throughout the growth to produce a flat top surface. With the proper equipment design, (aluminum-top hot plate and oil bath) other parameters were then investigated to optimize growth conditions.

26.9	26.5	25.7	28.3	29.0	31.0	30.9
34.0	42.8	47.4	56.6	41.4	39.7	38.6
45.4	64.7	71.8	74.8	73.1	65.8	51.4
49.8	67.2	75.3	77.8	75.3	69.8	55.6
49.2	68.8	76.1	78.0	75.8	71.0	58.4
50.8	68.9	77.1	78.0	75.9	71.2	59.1
47.1	64.9	75.3	74.9	73.3	69.3	54.3

Figure 4.2. Heat map for ceramic-top hot plate. Each square represents a temperature measurement in celsius for a 1 in.² area. Hot plate was set at 80 °C.

4.1.2. General Growth and Characterization of MAPbBr₃ Single Crystals.

In this section, general characterization of MAPbBr₃ single crystals will be presented. Figure 4.3 shows a picture of four different MAPbBr₃ single crystals grown via ITC growth technique. The squareness of the crystal depends on where nucleation begins in the vial. The top two crystals shown in Figure 4.3 began nucleation in the middle of the 20 mL, glass vial resulting in very square formation of the final crystal. Meanwhile, the bottom two crystals shown in Figure 4.3 began nucleation near the edge of the vial, which resulted in restricted directional growth forming with a longer length than the width. This yields potential for shape control of samples as shown in previous literature, where the shape of samples can be designed based on the shape of the container.⁵⁰ The transparency of the crystals shown in Figure 4.3 is indicative of low inclusions for high quality crystals. Solution-based crystal growth has proven advantageous as a simple, low-cost, and quick crystal growth technique. Although the growth of the crystal is dependent on the amount of precursor available in solution, which is limited by solubility, the ITC technique allows for the use of a grown single crystal as a seed in a fresh solution for larger growth. This is a process allowed by the fact that single crystals are formed by the highly-textured alignment of crystallites into the final single crystal, as reported by Chen, et al.⁶¹ Figure 4.4 shows a crystal grown with iterative ITC techniques to grow a larger volume single crystal. The crystal depicted in Figure 4.4(left) was grown after one cycle of the ITC method with a final volume of 56.99 mm³. The crystal shown in Figure 4.4(right) was grown after six iterative cycles using the previously grown crystal as the seed with a final volume of 301.41 mm³.

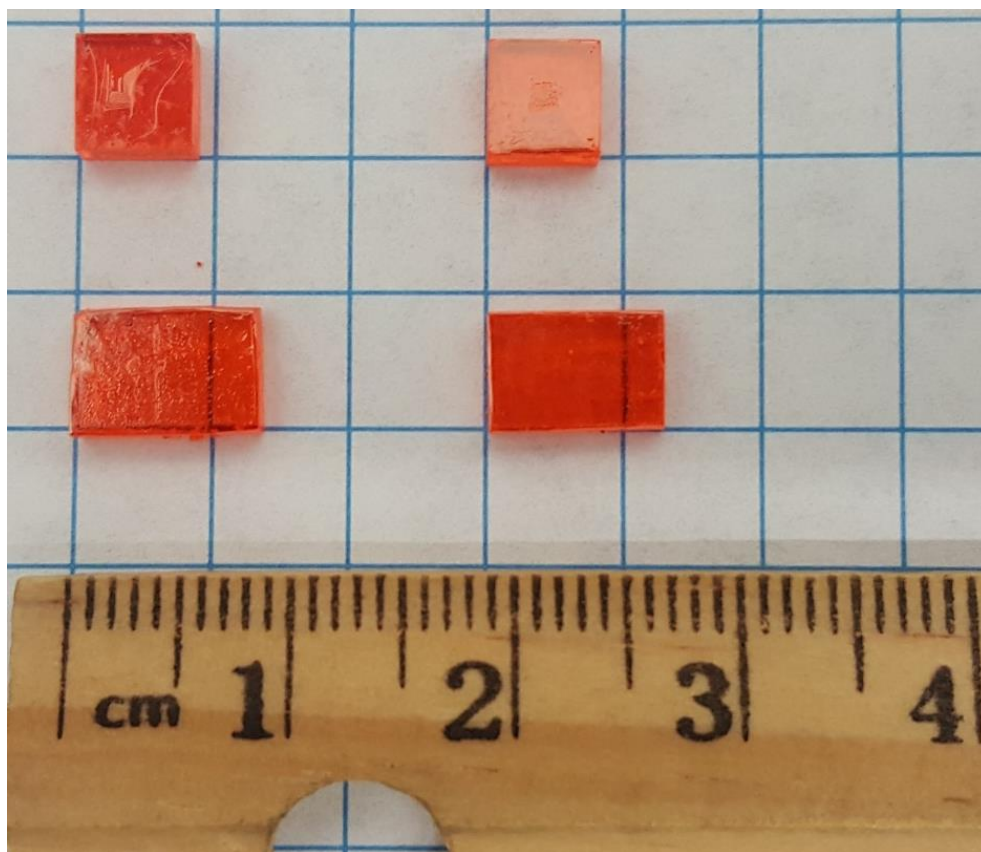


Figure 4.3. Picture of typical MAPbBr₃ single crystals grown via ITC method.

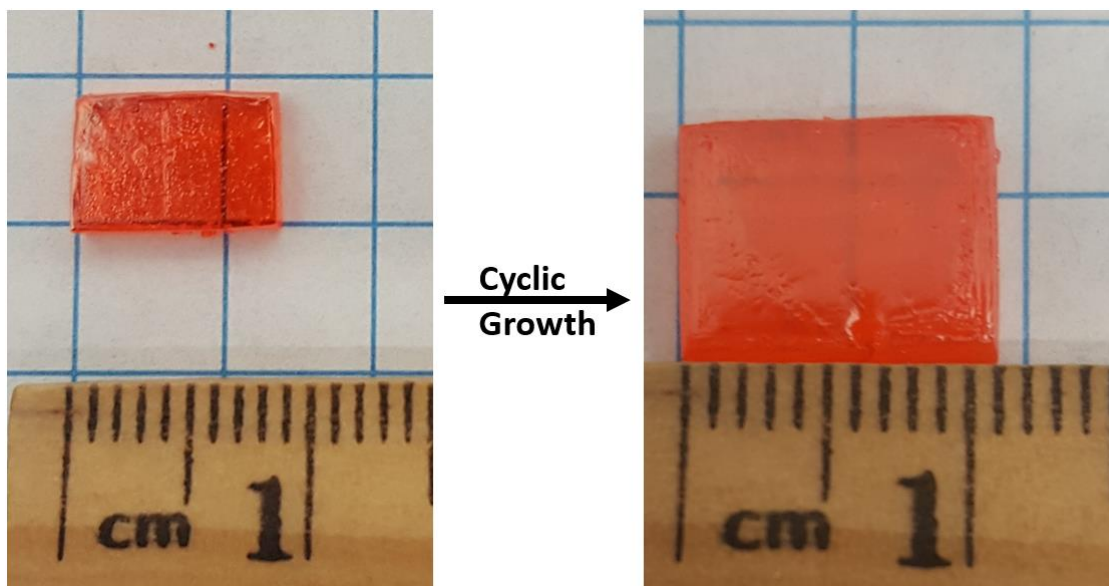


Figure 4.4. Depicting the use of cyclic growth to grow large volumes MAPbBr₃ single crystals via ITC iterative growth.

In this process, after the original single crystal has grown, the crystal is taken out of the heated DMF and placed on clean, absorbent paper to gently dab the excess DMF off the crystal surfaces. A fresh solution is preheated to ~ 20 °C below the final crystallization temperature, and the seed crystal is gently placed in the center of the new vial with fresh solution. Then, the solution with the seed crystal is heated at a rate of 20 °C/hr to the final crystallization temperature and left undisturbed for two to three hours while the growth occurs. This process is repeatable depending on the desired size of the final crystal, and then washed as previously discussed with DCM. Table 4-1 shows each iterative cycle for the iterative growth of the crystal pictured in Figure 4.4. The data in Table 4-1 shows that the crystal grew constant in each dimension during each cycle. This shows that the original shape of the seed crystal dictates the final shape of the final crystal after iterative growths. For each cycle, the crystal volume increased by an average of 48.89 mm^3 . This process allows for accurate control of the dimensions based on the seed crystal for any desired size based on application. However, optimization of this method could result in larger increase in volume per cycle. Figure 4.5 shows general XRD patterns for MAPbBr₃ single crystals. The powderXRD pattern, shown in Figure 4.5a, agrees with previous literature for MAPbBr₃ single crystals and the data confirms the samples are single phase (ICDD# 01-084-9476).⁶² All the characteristic peaks of the cubic $Pm\bar{3}m$ space group are observed, and the refined lattice parameter of $5.9300(2)$ was calculated from the XRD pattern. The Laue diffraction pattern, shown in Figure 4.5b, was recorded for the top surface of the MAPbBr₃ single crystal, (depicted in Figure 4.5c) confirming that the top surface of the crystal is perfectly aligned as the (100) crystallographic plane.

Table 4-1. Dimensions of MAPbBr₃ crystal grown via iterative ITC growth technique.

	Length (mm)	Width (mm)	Thickness (mm)	Volume (mm³)
Cycle 1	7.86	5.07	1.43	56.99
Cycle 2	8.70	6.10	1.88	99.77
Cycle 3	9.63	6.84	2.39	157.43
Cycle 4	10.35	7.71	2.74	218.65
Cycle 5	11.00	8.02	2.87	253.19
Cycle 6	11.69	8.77	2.94	301.41
Average	0.77	0.74	0.30	48.89

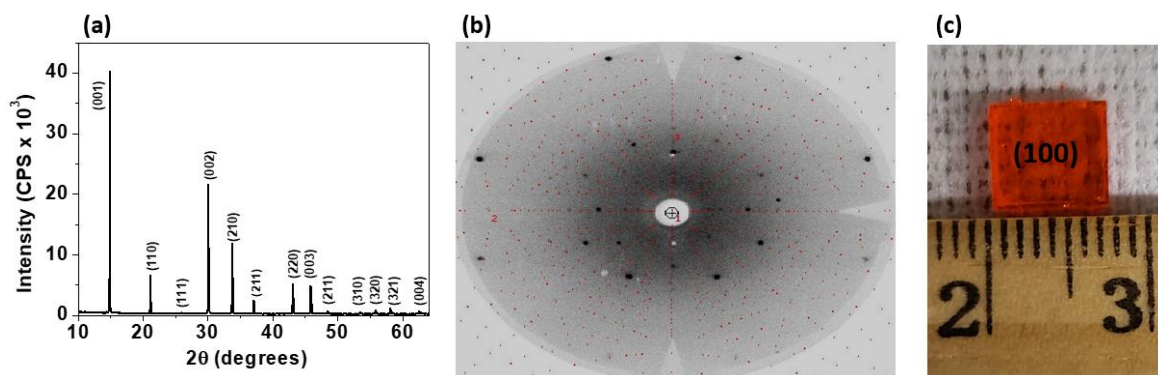


Figure 4.5. MAPbBr₃ single crystal (a) PowderXRD pattern (b) Laue diffraction pattern and (c) crystallographic plane orientation labeled on top surface.

Figure 4.6a shows the absorbance and normalized photoluminescence of a MAPbBr₃ single crystal. Although the exact values of these properties is not exact across all of literature, the absorption band edge position around 570 nm, the shape of the absorption curve, and the PL peak position are all in agreeance with literature values.^{50, 62-63} The PL of the grown MAPbBr₃ single crystal was measured under photoexcitation of a 405 nm continuous wavelength (CW) laser. The yellow-green photoluminescence of a high quality MAPbBr₃ single crystal can be clearly seen by eye under photoexcitation as seen in the inset of Figure 4.6a. This produces a PL spectrum with two different peak positions that are fit with Gaussian functions in Figure 4.6a. The major peak is located at 534 nm with a full-width half max (FWHM) of 21 nm. This peak originates from band-to-band recombination and is the predominant process in the PL of the material. The second, minor peak is located around 565 nm (FWHM = 17 nm). This peak appears much smaller, as a shoulder to the major peak. This peak is attributed to trap-assisted recombination below the optical band gap, which is due to Br⁻ vacancies at the surface.^{40, 64} This two peak PL spectrum gives a simple, qualitative analysis for quality of crystal surfaces by observing the relative intensity of the shoulder peak to the major peak. In this way, a relatively larger second peak gives comparative information alluding towards a higher amount of surface defects from bromine deficiency. Another important property of MAPbBr₃ single crystals derived from Figure 4.6a comes from the overlap observed, where the major peak from the PL spectrum is fully encompassed by the absorption spectrum. Here, it is shown that the PL emission from MAPbBr₃ is readily self-absorbed in the material, which poses issues for light emission signals in applications such as scintillation or LEDs.

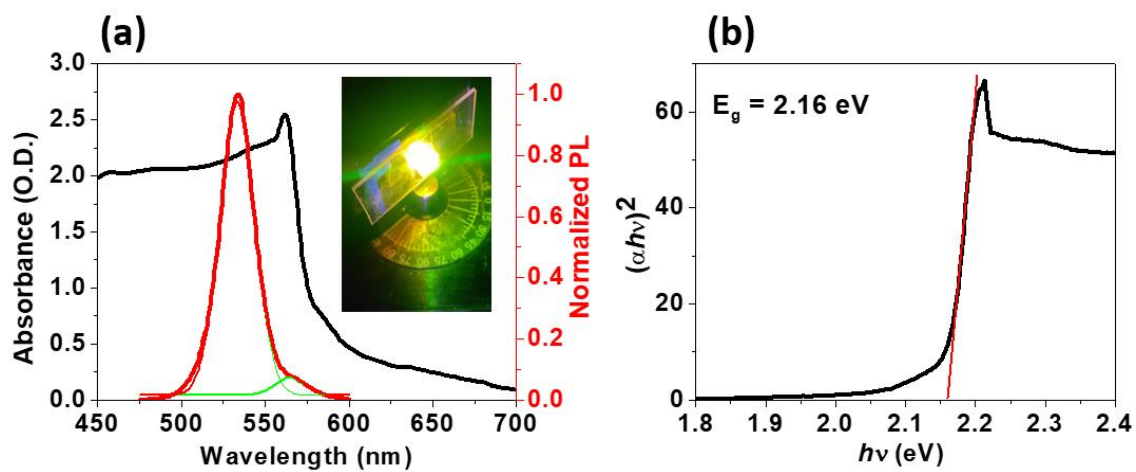


Figure 4.6. (a) Absorbance and normalized photoluminescence of MAPbBr₃ single crystal and (b) Tauc plot from absorbance to calculate band gap of MAPbBr₃ single crystal.

Figure 4.6b shows the Tauc plot for a MAPbBr₃ single crystal. This plot is derived from the UV-Vis absorption spectrum, where the optical density (O.D.) of absorbance is converted to $(\alpha h\nu)^{1/r}$ for the ordinate axis. In this conversion, the absorption coefficient, α , of the material can be related to optical density by dividing the optical density by the thickness of the material in cm, or by previously reported values of α for the absorber material. The absorption coefficient is then multiplied by the energy of light in eV and raised to the power of 1/r, where the value of r is determined by the type of semiconductor studied, and if the transition is allowed or forbidden.⁶⁵ Allowed transitions take place when angular momentum, energy, and linear momentum are conserved, resulting in direct transitions induced by a single photon process. These transitions are most likely to occur. On the other hand, when these quantum quantities are not conserved, forbidden transitions occur, which are transitions between states that require other interactions with additional particles involved, such as photons or phonons, and are less likely to occur. Here, $r = 1/2$ for direct band gap semiconductors with allowed transitions, $r = 3/2$ for direct band gap semiconductors with forbidden transitions, $r = 2$ for indirect band gap semiconductors with allowed transitions, and $r = 3$ for indirect band gap semiconductors with forbidden transitions. Therefore, $r = 1/2$ for MAPbBr₃ in the Tauc plot, as it is a direct band gap semiconductor and allowed, band-to-band transitions are used to estimate the optical band gap. The abscissa in the Tauc plot is simply the wavelength converted to energy of incident light by the relationship shown in Equation 4.1,

$$h\nu \text{ (eV)} = 1240/\lambda \quad (4.1)$$

where $h\nu$ is the energy of light in eV and λ is the wavelength of the incident light. When these are plotted together, the Tauc plot is formed. Then there is a sharp edge formed on the plot, where a tangent line is drawn and the intercept of the tangent on the x-axis is the optical band gap of the material. The band gap of MAPbBr₃ single crystal was estimated at 2.16 eV, which is in agreeance with the range of values reported in literature.⁶²⁻⁶³

4.1.3. Precursor Ratio Effects on MAPbBr₃ Single Crystal Growth

The next parameter investigated in the growth was the amount and molar ratio of precursors in solution. Many reports in literature discuss the use of different precursor amounts, but never give a detailed discussion of why the amount and ratios of precursors contributes significant differences in crystalline quality.^{50, 66} First reports on the growth of MAPbBr₃ crystals used an equimolar amount of PbBr₂ to MABr at a 1 M concentration in DMF. After development of this materials began, it was proposed that the use of a 0.8 ratio of PbBr₂ to MABr yielded single crystals of higher quality, which improved the $\mu\tau$ -product.²¹ Here, the effects of precursor ratio were further explored. MAPbBr₃ single crystals were grown with various precursor molar ratios of PbBr₂ to MABr including 1:1, 1:1.25, 1.25:1.5, and 1.5:1.5, all grown using DMF as the solution solvent. All solutions prepared, and crystals grown were done so using the ITC method, as described in section 3.1. One of the main observations with change in precursor ratio was the change in temperature path. When growing single crystals, the ramp rate of oil bath temperature plays an important role in growing one larger volume single crystal per vial, rather than simply growing many sub-millimeter size crystals. Here, the temperature path is defined as the ramp rate of the

temperature and the amount of time certain temperatures are held before ramping again. This temperature path is designed to help grow high quality single crystals with sharp edges and flat, parallel surfaces. The final temperature at which the single crystals have completed growth is referred to here as the final crystallization temperature. The final crystallization temperature is a function of crystallization thermodynamics discussed in section 1.5, depending on the inverse solubility for the precursors and mainly on supersaturation of precursors in solution. This is clearly shown by the results presented in Table 4-2, where the range of crystallization temperatures observed for different ratios is tabulated. When using a 1:1 molar ratio a crystallization temperature of 80-85 °C was observed through many growth cycles, in agreeance with the typical crystallization temperature reported for MAPbBr₃ single crystals.^{50, 62} As shown in Table 4-2, as the amounts of precursors in the solution increase, the crystallization temperature decreases down to as low as 50 °C for 1.5:1.5 M ratio of PbBr₂: MABr. The crystallization temperature decreases as the amount of precursors increases, because the supersaturation of the solution increases. There are a few benefits in increasing the amount of precursors in the solution. The decrease in crystallization temperature can lower the thermal stress applied to the sample during growth, reducing possibilities for microcracking during growth. Also, the decrease in crystallization temperature reduces the possibility of thermal shock when washing the sample, as it is transferred from the heated DMF to room temperature DCM to remove excess DMF. Also, because there is additional precursor in solution, larger volumes can be grown from the original crystallization cycle.

Table 4-2. Final crystallization temperature ranges for growth using different precursor ratios.

PbBr₂: MABr Molar Ratio	Crystallization Temperature (°C)
1:1	80-85
1:1.25	70-80
1.25:1.5	60-70
1.5:1.5	50-60

Table 4-3. Van der Pauw bulk resistivity measurements for MAPbBr₃ crystals with varying precursor ratios.

Precursor Ratio (Molar ratio)	Average Bulk Resistivity (GΩ-cm)	St. Dev. Bulk Resistivity (GΩ-cm)
1:1	4.86	1.03
1:1.25	11.34	0.82
1.5:1.5	6.23	1.66
1.25:1.5	9.03	0.83

Another important effect in changing the precursor ratio is the use of an offset molar ratio of 0.8 for PbBr_2 : MABr . Table 4-3 shows electronic properties of MAPbBr_3 single crystals grown with different precursor ratios based on the Van der Pauw bulk resistivity measurements described in section 3.3.2. Here, it is clearly shown that the average bulk resistivity of MAPbBr_3 single crystals grown with a 0.8 M ratio are higher than single crystals grown with equimolar solutions. This is due to the large difference of solubilities between MABr and PbBr_2 in DMF. The solubility of each precursors has been heavily studied and shows that the room temperature solubility of MABr in DMF (~ 2.6 M) is much greater than the solubility of PbBr_2 in DMF (~ 0.7 M).²¹ Because of this, in an equimolar solution of MAPbBr_3 , PbBr_2 precipitates out much faster than MABr as the single crystal solution is heated. This causes non-stoichiometric surfaces with MABr deficiency and limits the growth to PbBr_2 being the limiting reagent. By using the offset molar ratio of 0.8, there is always more MABr in solution to equalize the stoichiometry throughout the crystal (especially at the surface). This can also be seen visibly in the crystal, where the transparency of the single crystal is directly relatable to the quality of the crystal via inclusions seen through cloudiness of the sample.

4.2 Precursor Purity Effects on MAPbBr_3 Single Crystal Growth

In this section, the effects of precursor purity on the structural properties, growth, and electronic properties is investigated. To study the impact that growth conditions have on the quality of MAPbBr_3 single crystals (desire low trap density and high charge carrier properties), it is important to understand similar studies on MAPbX_3 thin films processes,

single crystal growth techniques for MAPbX₃, and mechanisms behind the crystal growth techniques. In thin film hybrid perovskites, studies have shown that the purity of PbX₂ precursors used in the preparation of solutions for spray-coating and spin-coating have a large impact on the film properties and electronic device performance. Impurities incorporated in MAPbI₃ films have shown to drastically decrease the quality of the thin films. One report observed that charge carrier lifetime can decrease, and non-radiative recombination can increase due to impurities in MAPbI₃ thin films. The use of higher purity PbI₂ in spin-coating solution increased the PCE of MAPbI₃ solar cells by an average of 3-4%.⁶⁷ Also, it was shown that the purity of PbI₂ had a direct impact on the crystallinity, grain size and grain boundaries in MAPbI₃ thin films.⁶⁸ Single crystalline MAPbBr₃ has been gaining attention for a cost-effective, novel use in high-energy radiation detection, with high crystalline quality using low-cost, low-purity precursors, such as 98% PbBr₂.²¹⁻²² However, the effects of higher purity precursors is important to understand for benefit-cost ratio for efficient radiation sensing.

In this section, MAPbBr₃ single crystals grown with 98% PbBr₂ (Alfa Aesar) and 98% MABr (Sigma Aldrich) are referred to as low purity samples. MAPbBr₃ single crystals grown with 99.999% PbBr₂ (Sigma Aldrich) and >99.5% MABr (Osilla and GreatCell Solar) are referred to as high purity samples.

XRD data at 300 K are shown for single crystalline (preferred orientation) and ground, polycrystalline powder MAPbBr₃ in Figures 4.7a and 4.7b, respectively. These patterns agree with previous literature for MAPbBr₃ single crystals and the data confirms the samples are single phase (ICDD# 01-084-9476).^{62, 69} XRD patterns on the as-grown low

purity and high purity samples show highly textured, preferred orientation in the 001 crystallographic orientation. Both samples have extremely sharp peaks (FWHMs of each sample are outside of the instrumental broadening) that deviate by only $0.001^\circ 2\theta$ between samples. However, the intensity of observed counts for high purity samples is about 40% greater (shown by the normalization of the patterns) (shown by the normalization of the patterns) than the intensity of the low purity samples. This means a higher number of diffracted X-rays in the high purity samples, alluding to a higher degree of crystallinity. Also, the tail broadening observed in the low purity sample is explained by microstructural Lorentzian broadening due to crystalline domain disorder.⁷⁰⁻⁷¹ After the XRD patterns were collected on the as-grown single crystals, the crystals were ground into polycrystalline samples, showing that all characteristic peaks of the cubic $Pm\bar{3}m$ space group are clearly observed. When the samples are ground, the crystallite size and preferred crystallographic orientation are removed from the samples, showing that there are little to no peak differences in the powderXRD patterns, as shown in Figure 4.7b. The refined lattice parameter of the high-purity and low-purity phase were identically matched at $5.9300(2)$ Å, indicating that there are no differences in chemical strain between the high and low purity samples, as differences in ionic radii from impurities would lead to minor/major changes in lattice parameters. Further, rocking curves were used to directly measure the crystalline quality and mosaicity of the high and low purity samples. Figure 4.8 shows high-resolution XRD (HRXRD) triple-axis rocking curves for low and high purity curves, with peak fits for FWHM values. The triple-axis coupled rocking curve for the high purity sample is shown in Figure 4.8b.

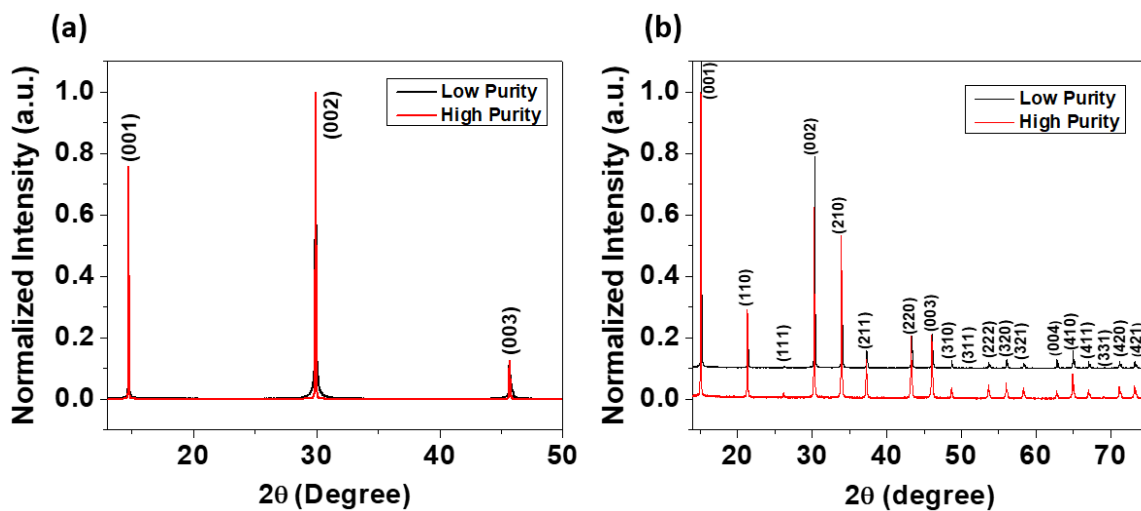


Figure 4.7. (a) XRD data collected on single crystals and (b) powder XRD for low and high purity grown single crystalline MAPbBr₃.

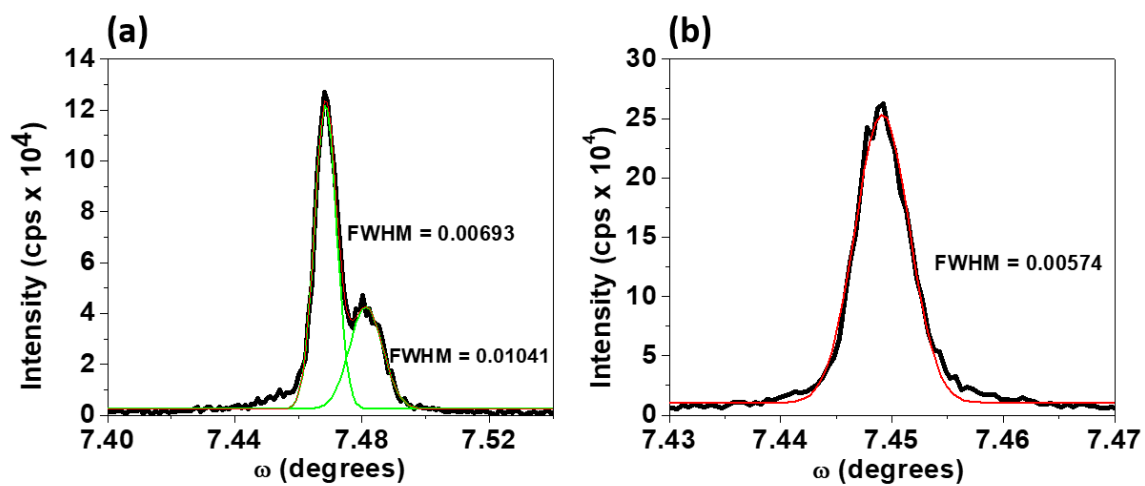


Figure 4.8. HRXRD triple axis rocking curves for (a) low purity and (b) high purity single crystalline MAPbBr₃.

This sample clearly shows only one, symmetric, sharp peak, (FWHM = 0.00574) which shows the sample has high crystalline quality, with highly textured alignment of crystalline domains and no plane tilting throughout the sample. Meanwhile, the low purity sample in Figure 4.8a shows a much different rocking curve, where the main peak (as compared to the high purity sample) is broader than the high purity sample (FWHM = 0.00693). The broadness of the main peak is attributed to disorder of crystalline domains (mosaicity) and a higher amount of defects than the high purity sample. Also, the rocking curve has an asymmetrical second peak with an even broader peak (FWHM = 0.01041). This second asymmetrical peak is attributed to plane tilting in the sample where the d-spacing in the low purity sample is mismatched due to defects, such as dislocations or domain mismatching.⁷²

Figure 4.9 shows Raman spectra for low purity and high purity samples. Raman spectroscopy was used to investigate the vibrational motions of the MA⁺ cations for high and low purity samples to study and differences in the organic framework of the single crystals. Each spectrum shows great signal to noise ratio, with sharp, high intensity peaks. Clear peak positions are observed at 915, 975, 1251, 1425, 1480, and 1590 cm⁻¹, all related to different MA⁺ cation motions as indicated in the work reported by Wang et al.⁶² For example, the 915 cm⁻¹ peak is due to CH₃NH₃⁺ rocking and the 975 cm⁻¹ peak is due to C-N stretching. The values of these peaks are in close agreement with reported Raman spectroscopy for single crystalline MAPbBr₃.^{5, 73-74} To make a direct comparison between the low and high purity single crystal MAPbBr₃ samples, the Raman spectra were

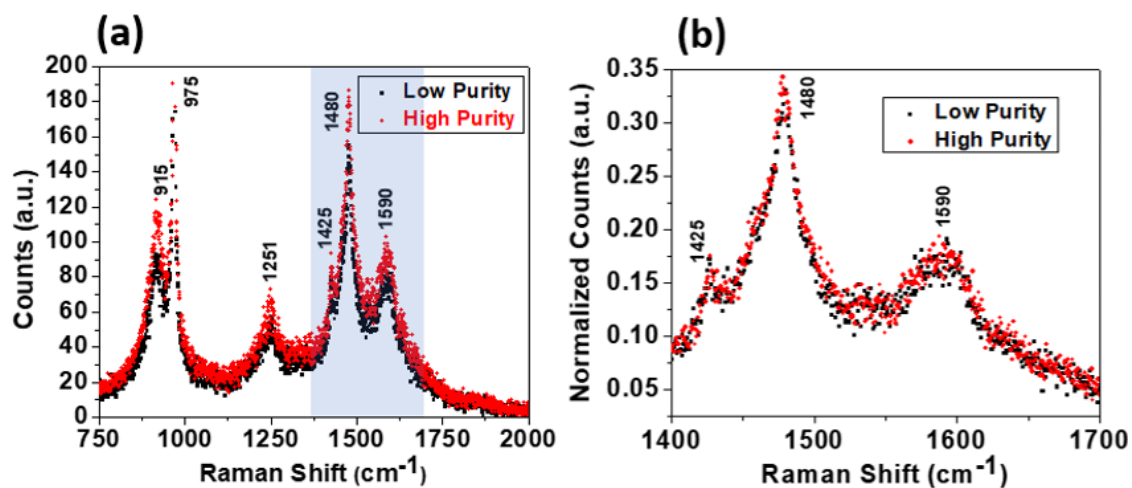


Figure 4.9. Raman spectroscopy for 98%-based and high purity single crystalline MAPbBr₃ from (a) 750-2000 cm⁻¹ and (b) normalized spectra from 1400-1700 cm⁻¹. (blue shading in 2a shows area of interest for 2b).

normalized, and the plotted range was decreased to the blue shaded region from Figure 4.9a, shown in Figure 4.9b. To make a direct comparison between the low and high purity single crystal MAPbBr_3 samples, the Raman spectra were normalized, and the plotted range was decreased to the blue shaded region from Figure 4.9a, shown in Figure 4.9b. Using peak fitting analysis, the largest deviations occur in peak area, possibly indicating more disorder in the low purity samples. However, peak positions are nearly identical, showing that the MA^+ cation motions were identical in each sample with no disturbances between samples.

Slight shifts in peak positions and widths, correlated to vibrational lifetimes, from reported values may arise from changes in sample crystallinity and defect composition. Therefore, due to the lack of any significant deviations when using lower purity precursor material, it is proposed that no large impurities are incorporated into the crystal structure that would alter the local environment of the organic framework. The high purity data does show that there is a higher intensity in the Raman spectrum as compared to the low purity data. From XRD and Raman analysis, using low purity precursors do not introduce any local or long range structural deviations correlated to the incorporation of impurities in single crystalline MAPbBr_3 ; however, using low purity precursors shows to have small effects on the alignment of crystalline domains and mismatching of d-spacing, where the high purity sample shows much better alignment of domains.

SEM images of the surface morphology are shown in Figure 4.10(a, b) for low purity samples and Figure 4.10(c, d) for high purity samples. SEM was used to physically show the particle size and alignment of crystalline domains between high and low purity samples.

The growth of MAPbBr₃ single crystals was directly studied by Chen, F., et al., where it is directly shown how crystallites align together in a highly-textured orientation to form the final cubic MAPbBr₃ single crystal.⁶¹ Further evidence is shown for this growth mechanism on the surface of the crystals, where square-like formations are observed as individual crystallites via SEM. Because solution-based growth of MAPbBr₃ forms single crystals through highly textured alignment of crystallites, it is important to understand impurity effects during growth, as impurities are able to act as nucleation sites, causing disorder in the alignment of crystallites.⁷⁵ The SEM images in Figure 4.10a depicts the low purity sample surface. The majority of the crystal surface texture consists of aligned crystalline domains on average of about 20-50 μm . However, there are areas of crystalline disorder, pictured in the zoomed-in region of interest in Figure 4.10b. This region contains much smaller crystallite domains in the range of 200 nm to 2 μm . This shows that a high amount of nucleation occurs with a lower amount of continual crystal growth in the crystalline domains, correlated to the presence of defect centers introduced by impurities from the lower purity precursors. Also, it is important to note that these small regions of crystalline domains appear more disordered and mismatched, which directly correlates to the rocking curves shown in Figure 4.8. Meanwhile, the SEM images of the high purity sample, shown in Figure 4.10(a, b), show much larger crystalline domains on an average of 100 μm and above (two to five times larger than low purity samples). When zoomed-in, there are no apparent regions of formation of smaller, disordered crystalline domains, as seen in the low purity sample. The mixture of reduction in the size of the larger micron-sized crystallites

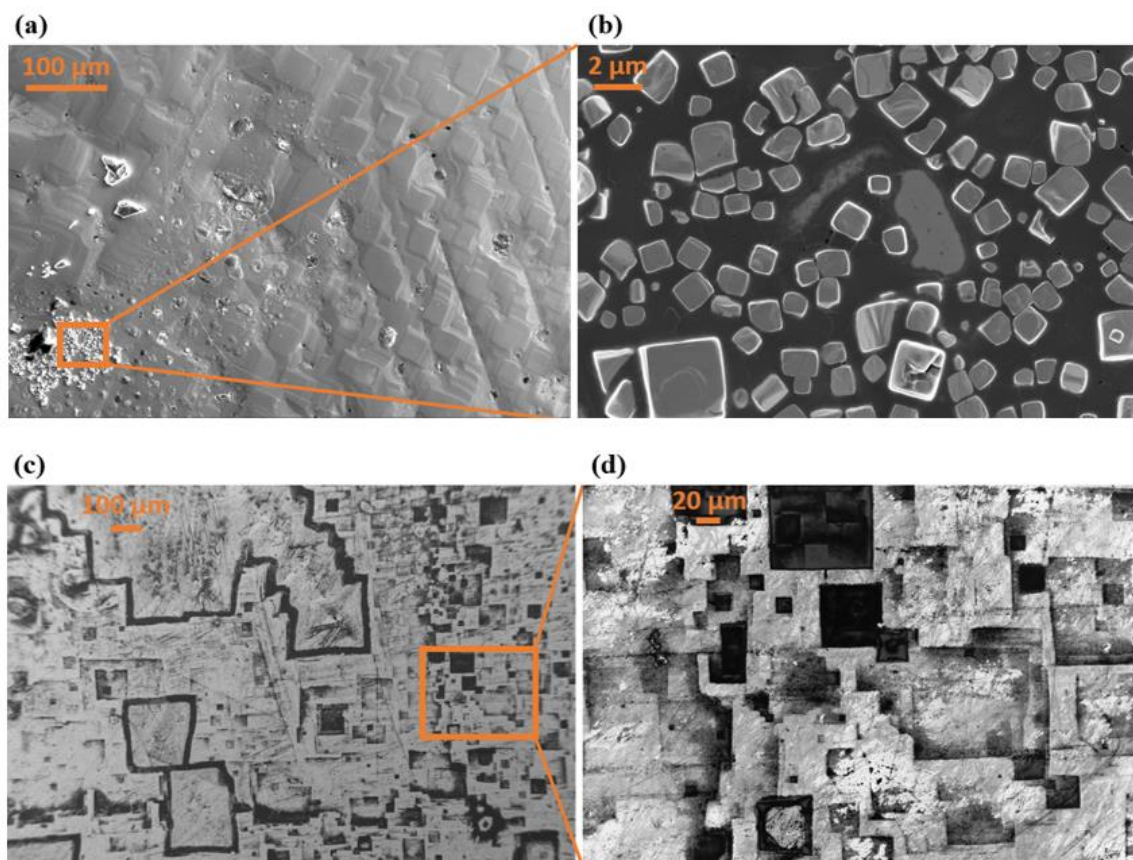


Figure 4.10. SEM images of (a,b) low purity MAPbBr₃ single crystals as-grown and (c,d) high purity MAPbBr₃ single crystals as-grown.

and the presence of nano-sized, disordered crystallites give rise to the peak changes observed between high purity and low purity samples in XRD characterization, as well as the differences in broadness and asymmetry in rocking curves. The decrease in crystallite size decreases the intensity of the diffracted X-rays and the presence of nano-sized crystallites leads to the Lorentzian broadening observed on the tails of the diffraction peaks. The disordered crystallites also give rise to more crystallite boundaries, which can act as trapping sites, adversely affecting electronic properties of the single crystal.

EDS (Figure 4.11) and ToF-SIMS (Figure 4.12) were used to ensure that the chemical composition remained homogenous throughout the surface of each sample despite the disorder and crystallite size of each region. EDS shows that the Pb to Br ratio was constant at a 1:3 ratio for both low and high purity samples regardless of the region of interest. ToF-SIMS also identifies a large peak for the methylammonium cation for both low and high purity crystals. This indicates that homogeneity of MAPbBr_3 is retained from small disordered crystallites to larger crystallite regions. Here, it is proposed that the changes in disorder of crystallites are caused by crystal growth in the presence of impurities. Although it is shown that impurities are not readily incorporated into the crystal structure, SEM shows that microstructural crystallite size and disorder changes when using low and high purity precursors. Using low purity precursors introduces more impurities in solution, which can act as nucleation sites.⁷⁵⁻⁷⁶ Therefore, in low purity samples, it is observed that a higher rate of nucleation happens with a lower amount of contiguous crystal growth, while high purity samples have less nucleation and more crystal growth.

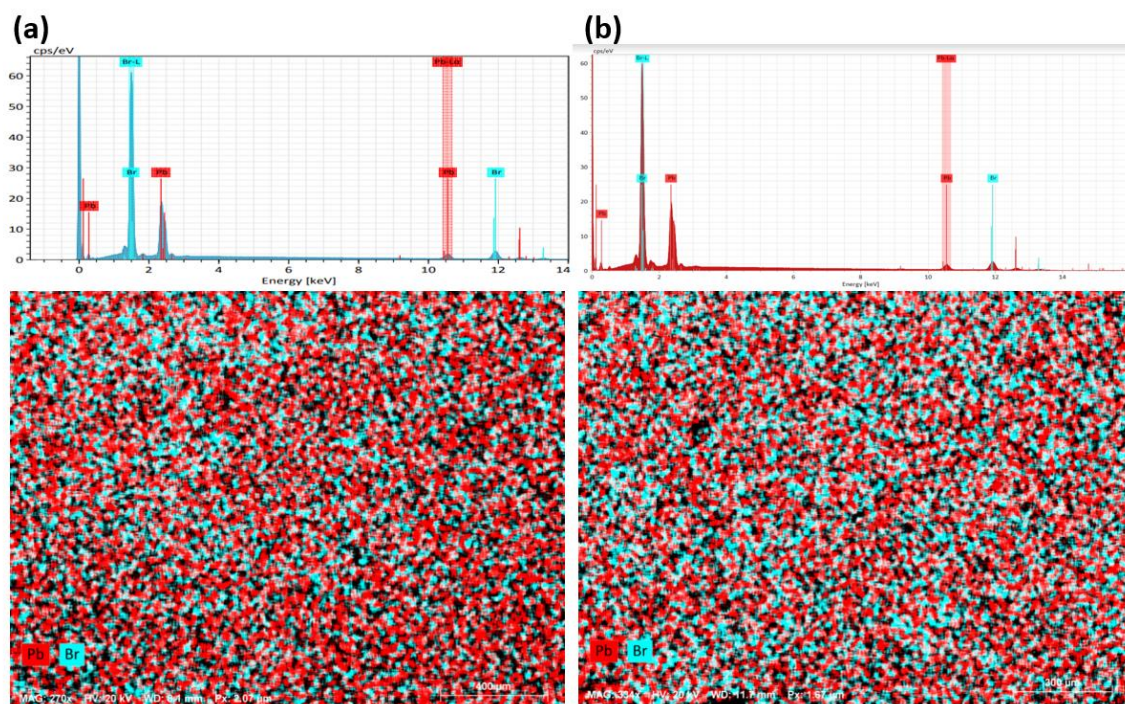


Figure 4.11. EDS energy spectra and map for Pb and Br content for (a) low purity MAPbBr₃ and (b) high purity MAPbBr₃ single crystals.

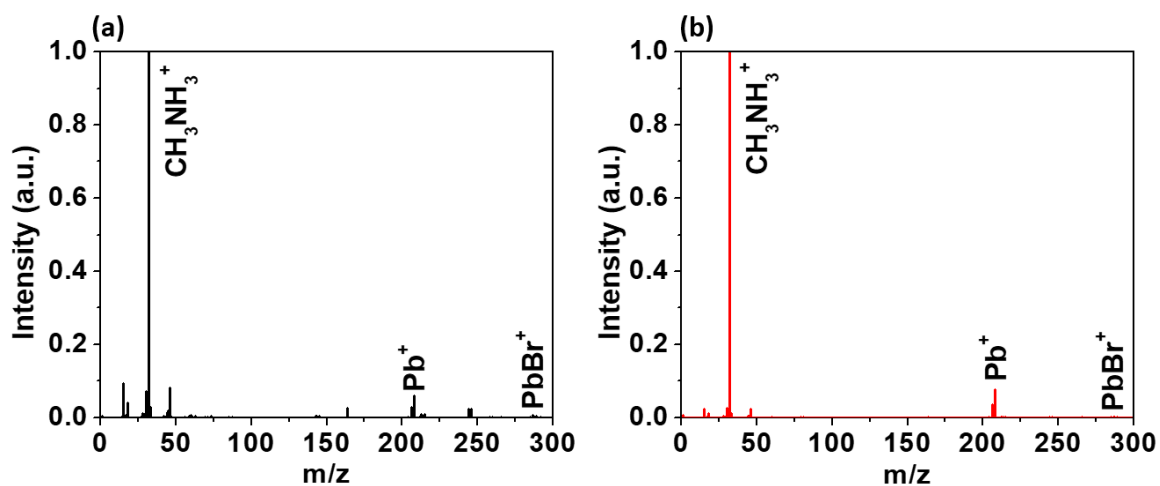


Figure 4.12. ToF-SIMS for MAPbBr₃ single crystals (key peaks labeled) showing the (a) 98%-based depth profile and (b) high purity depth profile. A Cs beam was used for the measurement; therefore, the Cs peak was removed for analysis.

ToF-SIMS positive ion mass spectrometry spectra are shown for MAPbBr₃ single crystals with low purity and high purity precursors in Figure 4.12a and 4.12b, respectively. For each sample, three key peaks were identified as CH₃NH₃⁺ (m/z = 32.05), Pb⁺ (m/z = 208.98), and PbBr⁺ (m/z = 286.89). Smaller peaks around CH₃NH₃⁺ were identified as other organic compounds, such as CH₂⁺ (m/z = 14.02) at lower values, and up to C₃H₉N₂⁺ (m/z = 73.05) at higher values. Br⁺ (m/z = 78.92) and ⁸¹Br⁺ (m/z = 80.92) were also identified in each spectrum. The low-intensity peaks are attributed to loosely bonded compounds in the MAPbBr₃ single crystals such as organic components bonded with Pb⁺ or Br⁺. Comparing the two ToF-SIMS spectra, there are small differences between the two precursor purities in elemental composition. However, the ToF-SIMS software analysis only identified the peaks of MA⁺, Pb⁺ and PbBr⁺, suggesting that impurities from lower purity precursors are not incorporated into the perovskite crystal structure when MAPbBr₃ single crystals are grown via ITC method. Other small peaks observed in the low purity samples may be attributed to the regions with poor alignment of nano-sized crystallites. Low impurity samples are grown, regardless of purity of precursors, due to solution-based crystal growth and stringent requirements for inclusions in the perovskite crystal structure. Unlike melt growths or solid growths, where any impurity in the stock material is incorporated into the final crystalline material, solution-based growth allows for impurities to be removed via filtering of the solution before growth and have less impurities incorporated through crystallization as impurities are left behind in the excess solution as the single crystalline MAPbBr₃ forms. This process is similar to purification of materials via recrystallization. Figure 4.13 shows the TRPL for low and high purity samples.

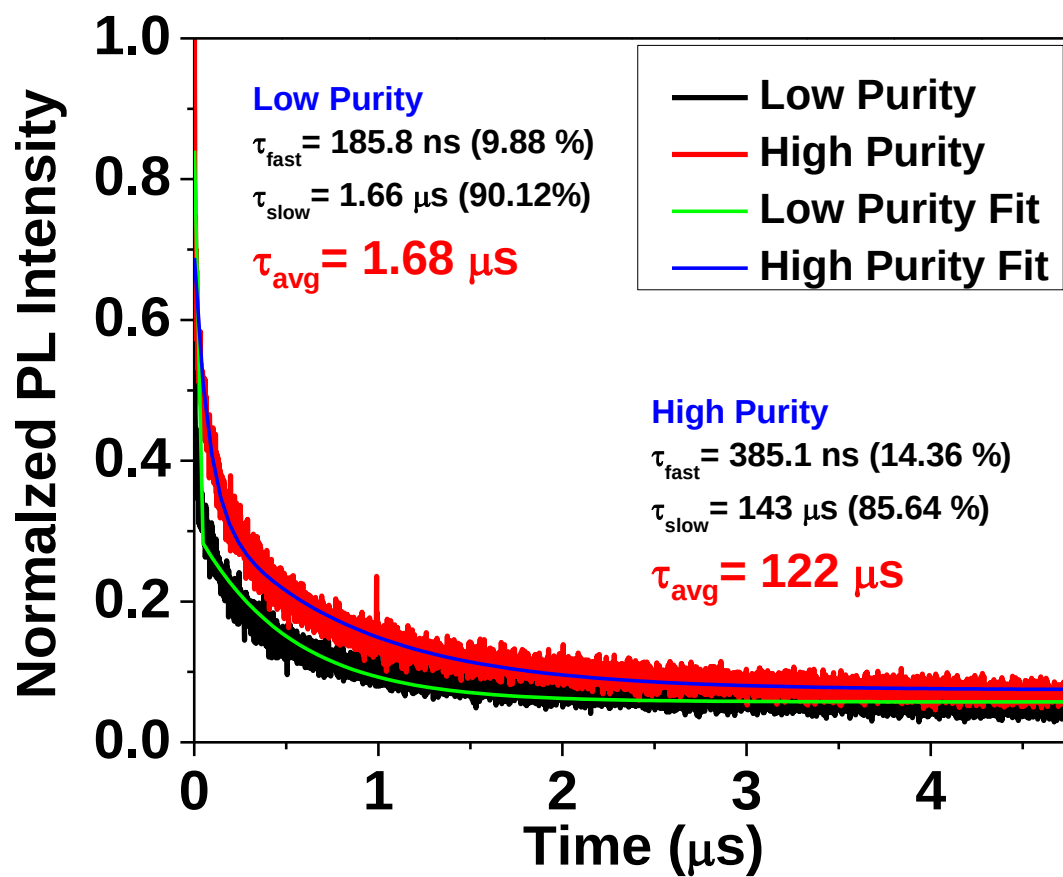


Figure 4.13. Normalized TRPL for MAPbBr₃ single crystals grown with low purity and high purity precursors.

Using TRPL optical dynamics in the MAPbBr₃ were investigated to understand differences in charge carrier lifetime and recombination processes.⁷⁷ A 370 nm nanoLED pulse photoexcitation source was used to probe the near-surface region of the samples.⁷⁸ Three samples of low purity and three sample of high purity MAPbBr₃ single crystals were measured and averaged to show reproducibility of the increase in charge carrier lifetime. For low purity, the charge carrier lifetime was calculated to be $\tau_{avg} = (1.26 \pm 0.36) \times 10^{-6}$ s, and for high purity, $\tau_{avg} = (1.18 \pm 0.12) \times 10^{-4}$ s. These values are attributed to carrier recombination processes at the near-surface region of the crystals, which directly affects the carrier diffusion length, where shorter charge carrier lifetime alludes to higher probability of e-h recombination and shorter carrier diffusion lengths. The high purity samples showed an increase of τ_{avg} by two orders of magnitude, indicating less nonradiative recombination and charge carrier trapping in the high purity samples.⁷⁸ The increase in charge carrier lifetime is attributed to the increase in crystalline domains and alignment in the high purity samples, where trap-assisted non-radiate recombination is less probable. On the other hand, in the low purity samples, the smaller, disordered crystalline domains may act as trapping centers, which increase the amount of charge trapping and probability of non-radiative recombination, negatively impacting charge carrier properties for efficient charge transfer. Enhancing the charge carrier properties is essential for radiation detection and optoelectronic applications, where low trap density and long diffusion lengths are desirable for efficient device performance. Therefore, it is shown that the high purity precursors can increase the size of crystalline domains, towards reducing charge trapping boundaries, enhancing charge transfer properties of single crystalline MAPbBr₃,

4.3 Effects of Ion Substitution

To solve the challenges of the OMHP single crystalline material, ion substitution/doping is used to enhance the electronic properties and performance of MAPbX_3 . Cationic substitution has been shown to tune phase stability in organic lead-iodide single crystals, where the MAPbI_3 crystal structure is tetragonal at room temperature, and the FAPbI_3 crystal structure is cubic at room temperature, but over time strain in the (111) plane of FAPbI_3 causes a phase transition from the α -phase to the non-perovskite δ -phase.⁷⁹ Therefore, many different allowing techniques have been used to stabilize the phase of iodide based OMHPs, such as the incorporation of the large organic cation ethylammonium (EA) into MA(EA)PbI_3 to dilate the lattice, driving the tolerance factor closer to one, for a stable cubic phase. The phase stabilizations are shown schematically in Figure 4.14. Also, the smaller organic cation methylammonium (MA) has been alloyed into FA(MA)PbI_3 to contract the lattice to reduce the sample strain.⁸⁰ MAPbBr_3 single crystals grow with a stable, room temperature cubic phase ($Pm\bar{3}m$). However, there are challenges that inhibit the performance of MAPbBr_3 -based radiation sensors, mainly the low, imbalanced electron and hole mobilities. As stated in section 3.3.2, SCLC is not an accurate measurement of the absolute value of hole and electron mobilities. Previous literature has reported a vast range of mobilities with this technique in OMHPs, as low as single digit mobilities for MAPbX_3 upwards to $600 \text{ cm}^2/\text{V} \cdot \text{s}$. Time of flight mobility measurements also tend to overestimate the absolute mobility of OMHPs, also being reported over $100 \text{ cm}^2/\text{V} \cdot \text{s}$

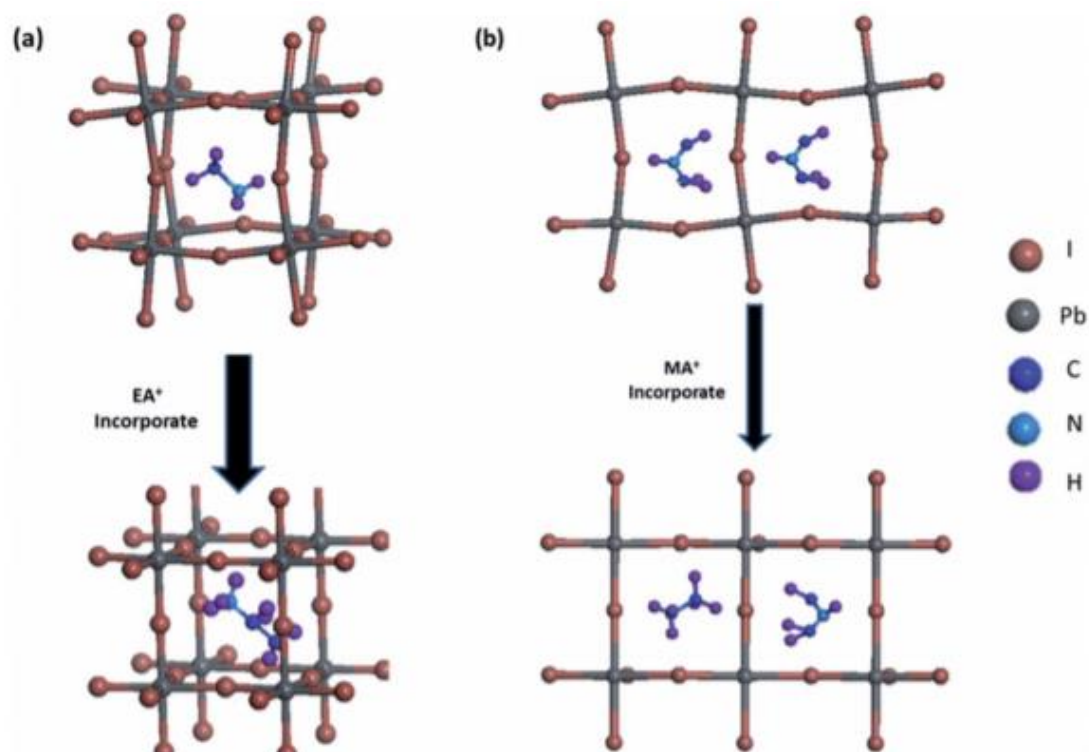


Figure 4.14. Schematic representation of lattice matching via organic cation substitution in (a) MA(EA)PbI₃ and FA(MA)PbI₃. Reproduced from ref. 80 with permission. Copyright 2018 RSC Advances.

for MAPbBr₃.^{48, 50, 63} These measurements tend to overestimate the true values of mobilities in OMHPs due to the well-known property of ionic conductivity in OMHPs.⁸¹ This leads to ion migration in perovskites, which creates electric-field screening effects and is the main concern for device hysteresis.⁸² Therefore, during the SCLC measurements, electro-migration from the external field can increase the mobility, causing an overestimation of intrinsic mobility. Also, time of flight measurements (photoexcitation and bias) can influence ion migration and combine this effect in the calculation of mobility values, due to electro-migration and photoinduced bulk polarization.⁸³ Therefore, the wide range of values for mobilities using these methods come from the effects of ion migration and polarization, which are inseparable from calculations of mobilities using these methods. However, here the SCLC method is useful to compare electron and hole mobilities for like devices. Hole only and electron only devices are created for these measurements and shown schematically in Figure 4.15, with their respective band diagrams. Band diagrams show the VB and CB values for each material in a layered structure and how they are aligned. Electrons flow from high to low values of the conduction bands (as CB and VB values are negative relative to vacuum). Holes flow from low to high values of the valence bands. Because MAPbBr₃ is dominated by hole transport, (p-type behavior) the device structure Au/MAPbBr₃/Au (Figure 4.15a) allows for holes to dominate the electronic properties for direct measurement of hole mobility. Meanwhile, the device structure in Figure 4.15b only allows for electrons to travel through the interfaces, while blocking hole transport, due to the band alignment of C₆₀ and MAPbBr₃ forbidding the transport of holes through the interfaces. This is shown schematically in Figure 4.16, where C₆₀ is a well-known electron

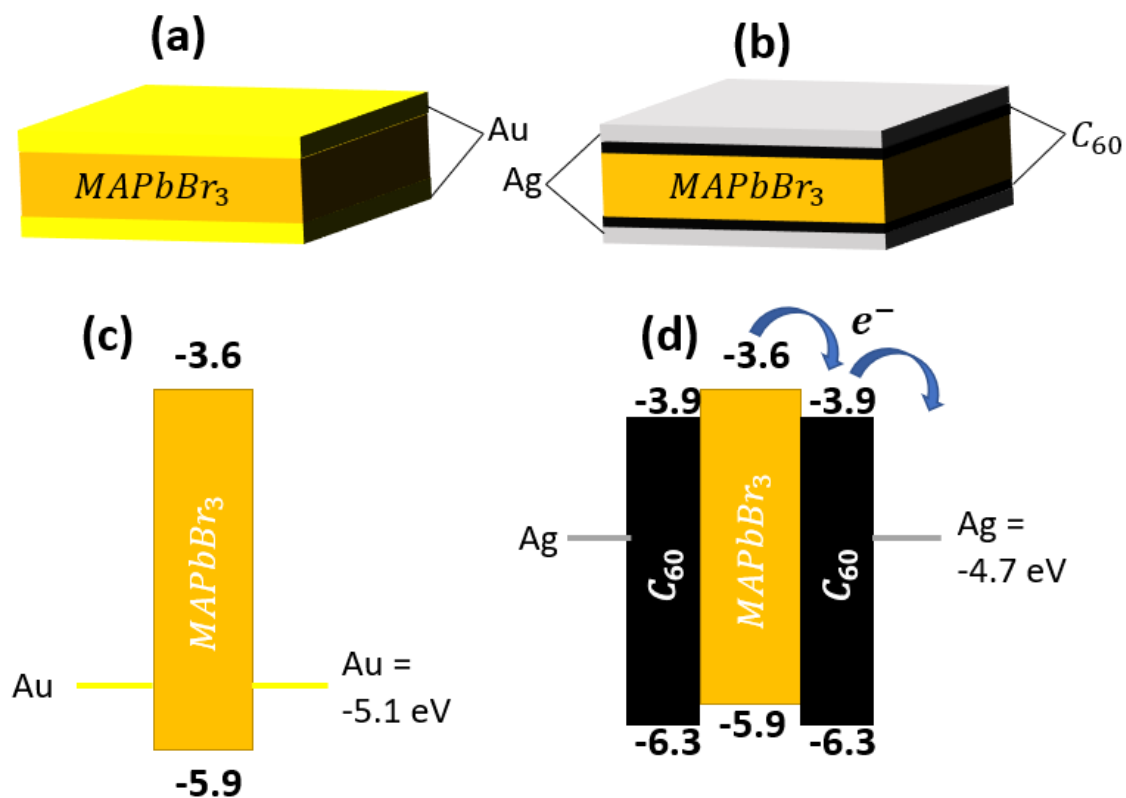


Figure 4.15. Schematic representation of MAPbBr₃ device structures for (a) hole only and (b) electron only devices for IV characterization. Band diagram for (c) hole only and (d) electron only devices. (Values for bands are units of eV)

transport layer, (ETL) which will be discussed in more detail in Chapter 5. This allows for direct measurements of electron mobility.⁶⁶ Using devices structures from 4.15, the SCLC hole mobility was estimated to be $185.2 \text{ cm}^2/\text{V} \cdot \text{s}$, and the SCLC electron mobility was estimated to be $82.2 \text{ cm}^2/\text{V} \cdot \text{s}$, showing that the electron mobility is over a factor of less than the hole mobility. The trap density between the hole only and electron only devices is similar ($n_{\text{trap},h} = 5.54 \times 10^9$ and $n_{\text{trap},e} = 5.24 \times 10^9$), which shows that the crystals used for each device are comparable and the change in mobility is in fact due to separation of electrons and holes, rather than the quality of single crystals used for the separate devices structures. These values are also promising to see that the trap density of these OMHP semiconductors are much lower than the trap densities of traditional inorganic semiconductors, such as Si ($n_{\text{traps}} = 10^{13} - 10^{14} \text{ cm}^{-3}$),⁸⁴⁻⁸⁵ CdTe ($n_{\text{traps}} = 10^{11} - 10^{13} \text{ cm}^{-3}$),⁸⁶ CIGS ($n_{\text{traps}} \approx 10^{13} \text{ cm}^{-3}$),⁸⁷ etc. The difference in electron and hole mobility is comparable to previously reported differences.^{22, 66} A more accurate estimation of mobility comes from the Hall mobility described in Figure 3.9b. The Hall mobility calculated for MAPbBr₃ was $70.93 \pm 10.44 \text{ cm}^2/\text{V} \cdot \text{s}$, which agrees with literature.⁵⁷

In radiation sensing, the balance of electron and hole transport is important to remove position dependence from the amount of charge collected. To increase the charge transport and bring equilibrium to the electron and hole mobilities, anion substitution has been proposed and shown to increase both transport mechanisms while balancing the values of each mobility.²² Figure 4.16 shows the effect of anion substitution, by replacing a small amount of Br with Cl to grow MAPbBr_{3-x}Cl_x single crystals.

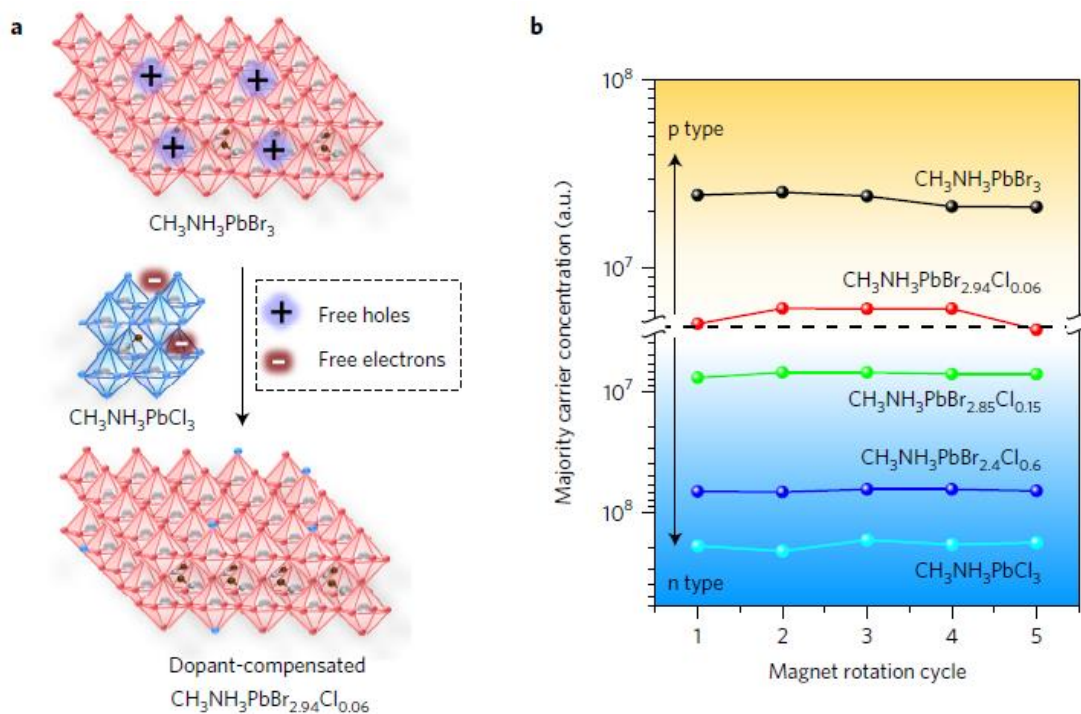


Figure 4.16. Cl^- alloying for $\text{MAPbBr}_{3-x}\text{Cl}_x$ single crystals. (a) Schematic of substitution on free charges, (b) Hall effect results to characterize the majority carrier type/concentration. Reproduced from ref. 22 with permission. Copyright 2017 Nature Materials.

From Figure 4.16, the Cl^- alloying effectively balances the majority charge carrier concentration to a more intrinsic behavior. This is because MAPbBr_3 is p-type (higher hole carrier concentration attributing free holes), while MAPbCl_3 is n-type (higher electron carrier concentration attributing free electrons). By substituting small amounts of Cl^- to grow $\text{MAPbBr}_{3-x}\text{Cl}_x$ single crystals, the p-type property of MAPbBr_3 and n-type property of MAPbCl_3 combine to create a more charge-balanced material. Because of this, a simple method for doping was adopted to grow $\text{MAPbBr}_{3-x}\text{Cl}_x$ single crystal for balanced charge transport towards developing efficient gamma-ray sensors. In this growth method, small amounts of MACl were dissolved in DMF solution containing PbBr_2 and MABr precursors. In this way, the Cl^- atoms in solution can be incorporated into the crystal structure as the atomic radius and charge are similar to Br^- ($r_{\text{Br}^-} = 1.85 \text{ \AA}$, $r_{\text{Cl}^-} = 1.75 \text{ \AA}$). When using MACl as the alloying precursor, MABr was replaced. For example, to grow $\text{MAPbBr}_{2.94}\text{Cl}_{0.06}$ single crystals, the molar ratio of PbBr_2 : MABr : MACl was 1:0.94:0.06 in DMF solution. Then the ITC method for crystal growth was carried out as previously described. With small amounts of alloying, the lattice constant, absorption band edge (band gap), and PL peak position and curve shape have all been shown to shift as a function of x in $\text{MAPbBr}_{3-x}\text{Cl}_x$, as shown in Figure 4.17. Because of these experimentally identified shifts, it is clear to understand if the doping mechanism used is efficient for the amount of MACl dissolved in solution, to the amount of Cl^- incorporated into the crystal structure.⁵⁹

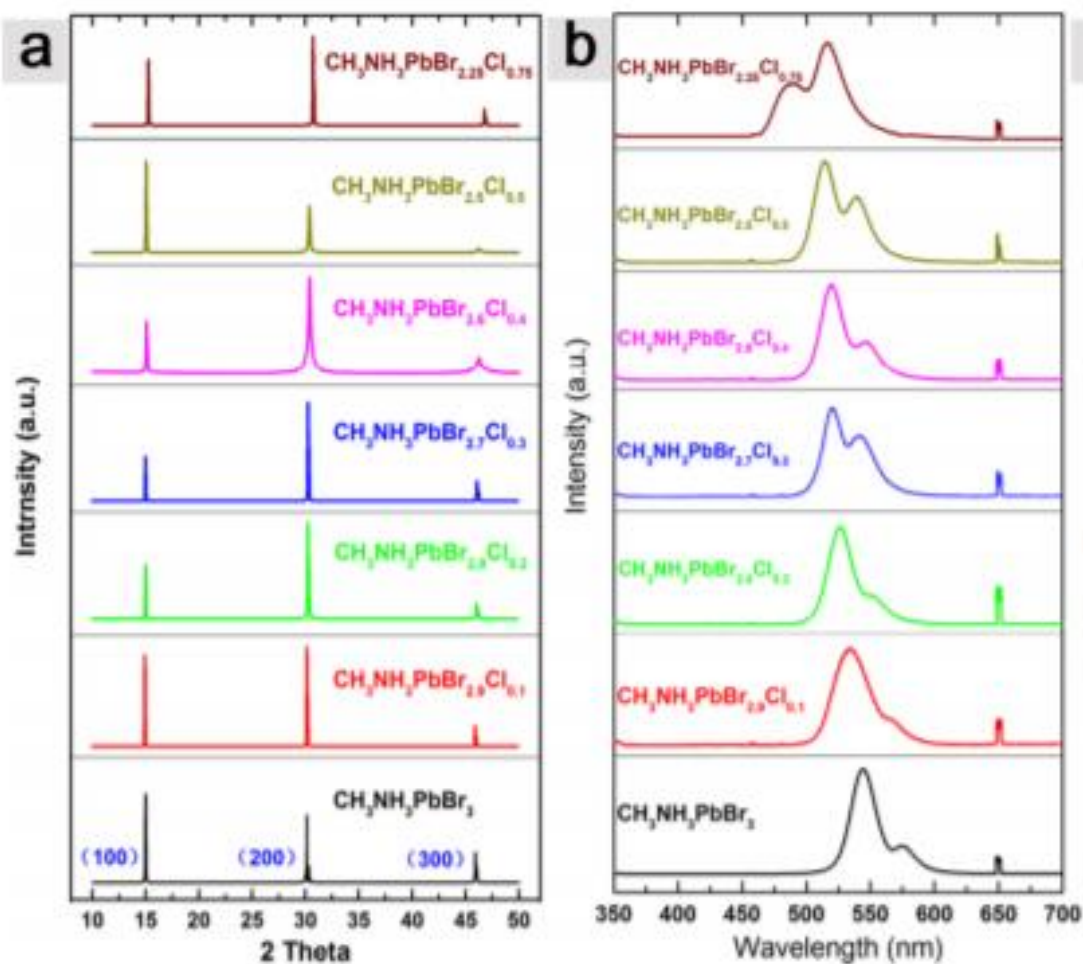


Figure 4.17. Shifts in (a) XRD and (b) PL spectra for MAPbBr_{3-x}Cl_x single crystals as a function of x . Reproduced from ref. 59 with permission. Copyright 2016 AIP Advances.

Figure 4.18a shows PL of MAPbBr_{3-x}Cl_x single crystals where x = 0, x = 0.06, and x = 0.15 for Cl⁻ doping of 0 at%, 2 at%, and 4 at%. The major peak in PL is compared in Figure 4.18 to the known blue shift phenomenon when MAPbBr₃ is doped with Cl⁻. The MAPbBr₃ peak position at 543 nm blue shifts to 536 nm with 2 at% Cl⁻ and further blue shifts to 533 nm with 4 at% Cl⁻, as expected. Also, the FWHM of the peaks and little to no apparent presence of the second trap-assisted peak, alludes to the growth quality of MAPbBr_{3-x}Cl_x is unaffected by the MAcl dopant precursor. HRXRD patterns were also collected on the (001) and (003) peak with and without 4 at% substitution of Cl⁻, as shown in Figure 4.18(b, c). With Cl⁻ doping, both diffraction peaks shift to the right, which indicates a smaller lattice constant (expected from previous literature).⁵⁹ Knowing the cubic phase of the material, the average lattice parameter, a, calculated from these peaks is derived from Bragg's Law in Equation 3.9, by relating the d-spacing to the crystallographic plane and lattice parameter as shown in Equation 4.2.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (4.2)$$

Using this method for comparison, the average lattice parameters calculated were $a_{MAPbBr_3} = 5.924 \text{ \AA}$ and $a_{MAPbBr_{2.88}Cl_{0.18}} = 5.917 \text{ \AA}$. These observations show that the Cl⁻ doping mechanism via inclusion of MAcl in the MAPbBr₃ solution is an effective method for MAPbBr_{3-x}Cl_x single crystal growth. In Chapter 6, devices based on MAPbBr_{3-x}Cl_x are further discussed and characterized for radiation sensing performance.

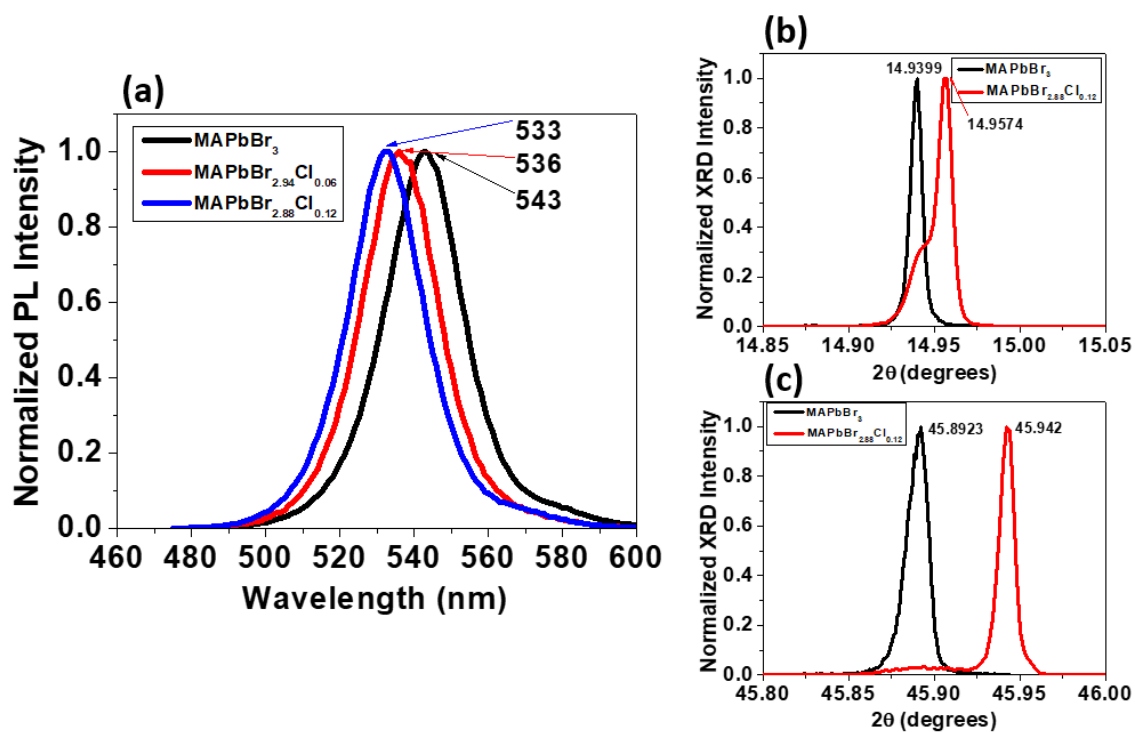


Figure 4.18. Photoluminescence for MAPbBr_{3-x}Cl_x single crystals with $x = 0$, $x = 0.06$, and $x = 0.12$. (b, c) HRXRD patterns with and without 4 at% Cl⁻ doping on the (001) and (003) crystallographic planes, respectively.

4.4 Photoinduced Effects on MAPbBr₃ Single Crystals

Photoinduced phenomena have been clearly shown in OMHPs affecting charge transfer properties. Reports have shown that photoexcitation can cause photoinduced bulk polarization in OMHP thin films and reduce the energy barrier towards more efficient charge transfer processes.⁸³ Studies on photoinduced lattice expansion (through unit cell dilation) has also been shown to enhance photovoltaic performance in OMHP thin films.⁸⁸ This work is further expanded upon here to understand photoinduced effects on structural and optomechanical properties in single crystalline MAPbBr₃. Figure 4.19 shows laser-dependent HRXRD measurements in MAPbBr₃ focused on the (001) and (003) crystallographic planes to compare changes in lattice parameters. Here, the average lattice parameters calculated were $a_{dark} = 5.924 \text{ \AA}$ and $a_{photoexcited} = 5.928 \text{ \AA}$. Larger percentage of lattice expansion phenomena has been shown in thin film OMHP. Since the material studied here is in single crystalline form, and a stable, cubic phase at room temperature, the smaller percent change in lattice with photoexcitation is expected. This photoinduced lattice expansion was also studied via Resonant Ultrasound Spectroscopy (RUS) to understand photoinduced effects on the elasticity of single crystalline MAPbBr₃. The RUS spectra shown in Figure 4.20 shows that the photoexcitation increases the bulk modulus and strengthens the material, observed by the shift in spectrum to the right.⁸⁹⁻⁹⁰ Here, it is shown that the photoinduced lattice expansion results in an increase in the bulk modulus of the material.

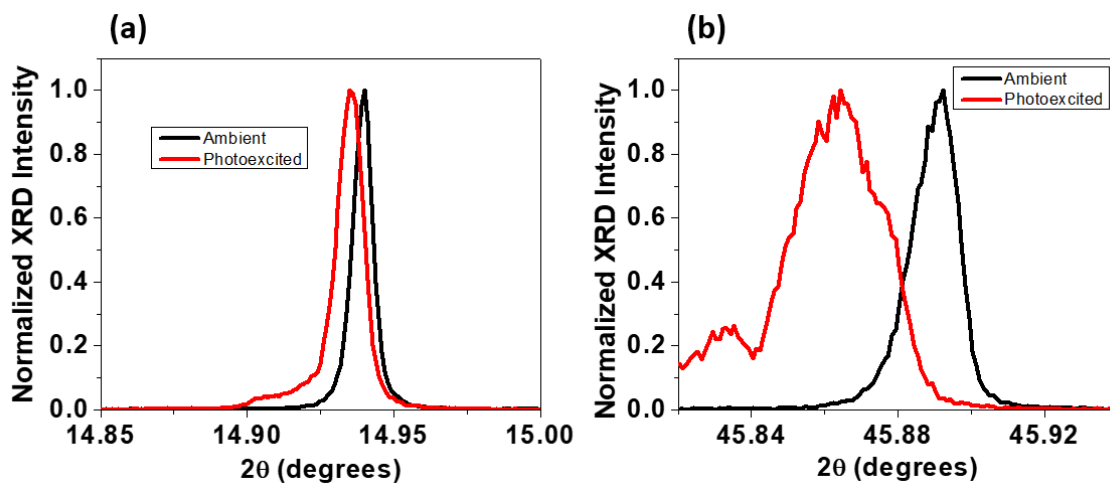


Figure 4.19. HRXRD patterns on MAPbBr₃ single crystals with and without a 405-nm laser photoexcitation on the (a) (001) and (b) (003) crystallographic planes.

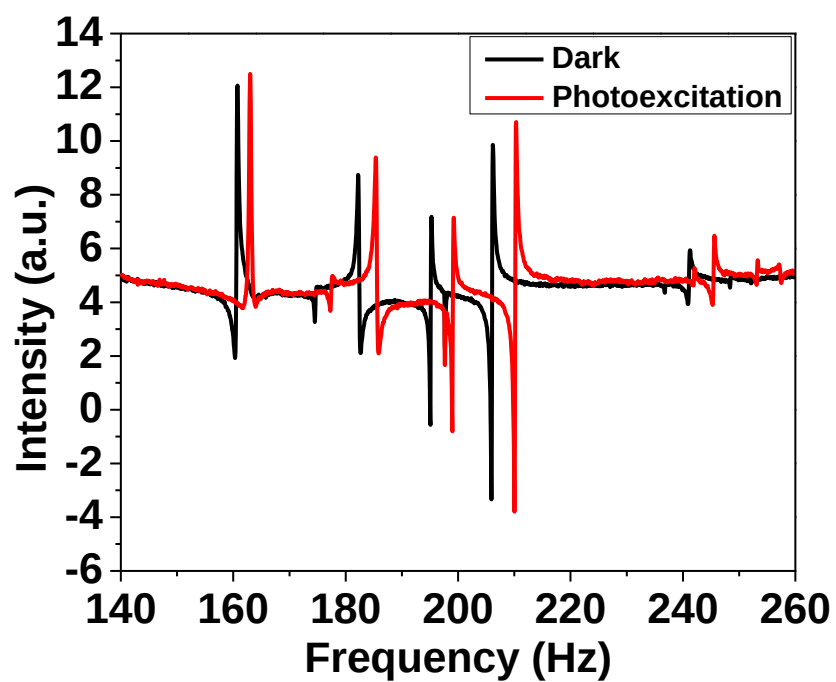


Figure 4.20. RUS spectra for MAPbBr₃ single crystals in dark and photoexcited conditions. (Photoexcitation source was 405 nm CW laser.)

5 Characterization of Devices

In this chapter, device fabrication and characterization of the devices will be discussed. Section 5.1 will discuss the importance of device design for OMHPs for radiation sensing. Section 5.2 will present the results on electrode selection for OMHP devices for sensing and optoelectronic applications.

5.1 Device Structure and Characterization

In typical device structures, many interfacial layers can be used to direct charge transfer processes towards specific electrodes, which is called interfacial engineering. This is very important in OMHP-based devices due to typical intrinsic p-type and n-type behavior of many hybrid perovskites. An energy diagram of a basic OMHP optoelectronic device energy diagram is shown in Figure 5.1. The band alignment of interfacial materials is crucial for designing devices with built-in electric fields to promote proper charge transfer throughout the device. The active layer in the middle is the OMHP material (thin films or single crystalline). When an incident photon interacts with the active layer, (light absorbed, or ionization via high-energy radiation) and electron-hole pair is created (either as an e-h pair, known as an exciton, or a free electron and hole). If an exciton is formed, dissociation of the exciton must happen to create the free electron and hole. Once the free charges are created, two layers on either side of the device play important roles. Electron transport layers (ETL) are band aligned in such a way to promote electron transport through the interface, while blocking hole transport. On the other hand, hole transport layers (HTL) are band aligned to promote hole transport through the interface with the active layer, while inhibiting electron transport. Then anode and

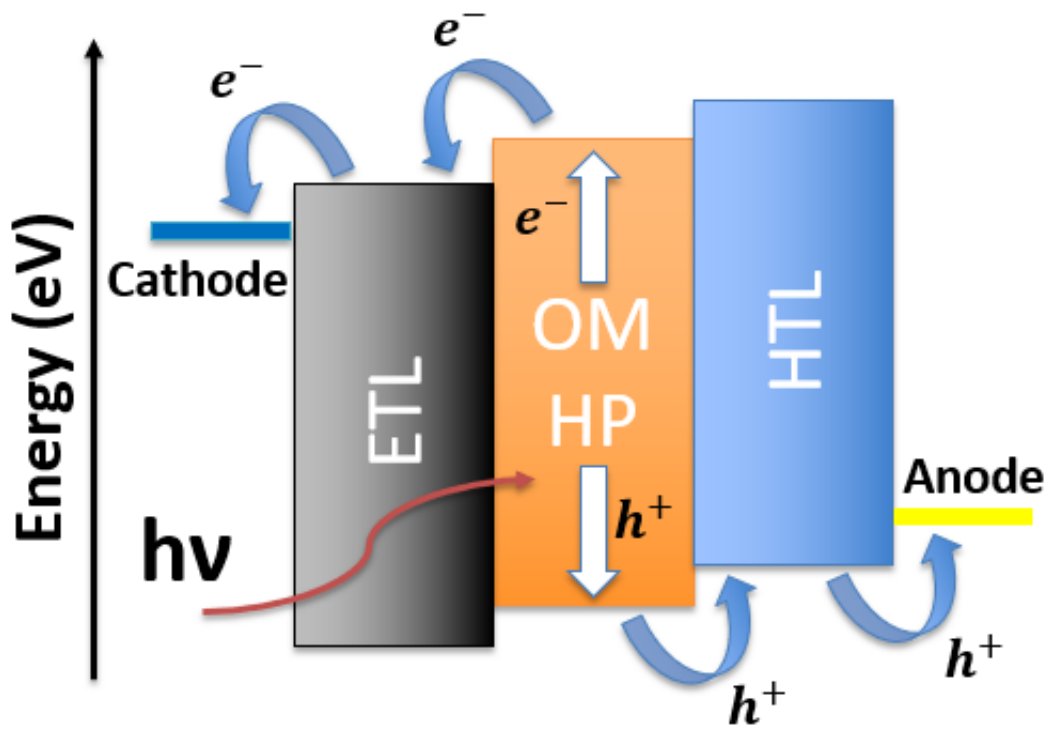


Figure 5.1. Energy diagram of typical OMHP device structure.

cathode can be aligned close to the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) on their respective transport layers; however, this electrode alignment is more crucial in terms of energy barriers rather than band alignment. Also, large band gap ultra-thin, passivation layers can typically be used in between the interfacial layers and electrodes to improve the interface between transport layers and metal electrodes.

For radiation detection device structures, the out-of-plane device architecture was used with interfacial layers and electrode structure of Cr (60 nm)/BCP (8 nm)/C₆₀ (20 nm)/MAPbBr₃/Cr (60 nm). This device structure in this work is shown schematically in Figure 5.2 along with the energy band diagram. This device structure is known as a hole-transport-layer-free due to the fact that the anode metal is in direct contact with the MAPbBr₃ semiconductor. In an HTL-free device structure, only the ETL is used. This is a typical structure type in MAPbBr₃ device structures due to the intrinsic p-type behavior, where hole carrier concentration and mobility is higher than the concentration/mobility of free electrons. Therefore, to help balance the charge transfer properties of holes and electrons, the ETL is placed in between the MAPbBr₃ single crystal and cathode to promote electron transfer, but the HTL is left out, since the hole transport properties are already dominant. HTL-free devices have many advantages including decrease in cost from using less materials, as well as the decrease of deposition of layers. These device structures have shown to provide efficient PCEs,⁹¹⁻⁹² and they have also been used in previous literature for high-energy radiation detection.^{20, 22}

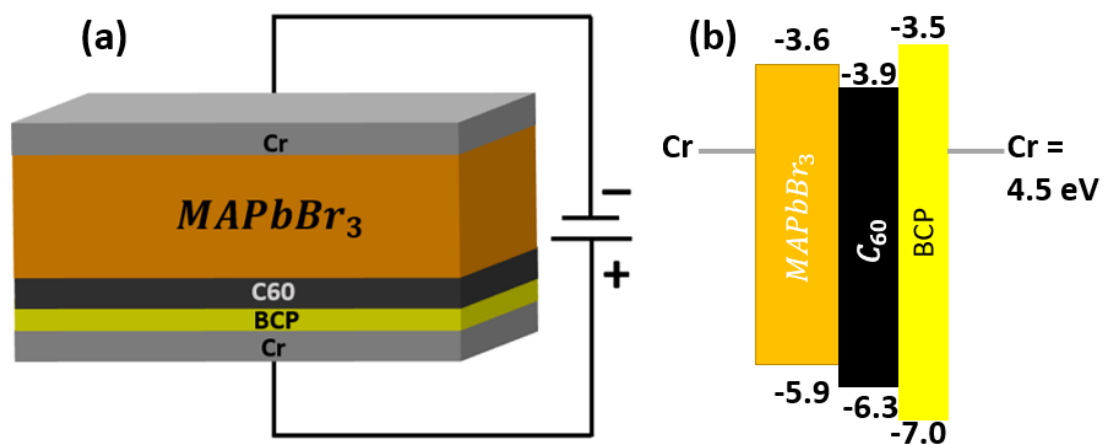


Figure 5.2. (a) Schematic representation of radiation detection device structure. (b) Energy band diagram of MAPbBr_3 device.

Thermal evaporation was used to deposit all layers and electrodes on MAPbBr₃ devices. First, the 20-nm C₆₀ ETL is deposited on the surface of the MAPbBr₃ crystal. After, the 8-nm BCP passivation layer is deposited on the C₆₀. The cathode is finally capped off with the 60-nm layer of Cr, and the anode is deposited by a single, 60-nm layer of Cr. The IV characteristics of the device structure is shown in Figure 5.3. The IV scan of devices (very small error bars shown in red) shows an ohmic contact, with linear behavior from 0 to 100 volts. The average resistance of the device was calculated to be $R = 1.12 \pm 0.02 \times 10^9 \Omega$. The device resistance is on the same order of magnitude as the Van der Pauw measurements shown in Table 4-3, which shows that the contact resistances do not adversely affect the overall resistance of the device. The ohmic, high resistive IV characteristics of the device are desirable for detection of high-energy radiation detection, as this detector is operated in current mode, which requires high resistance materials to process the low signal generated from high-energy radiation interactions.

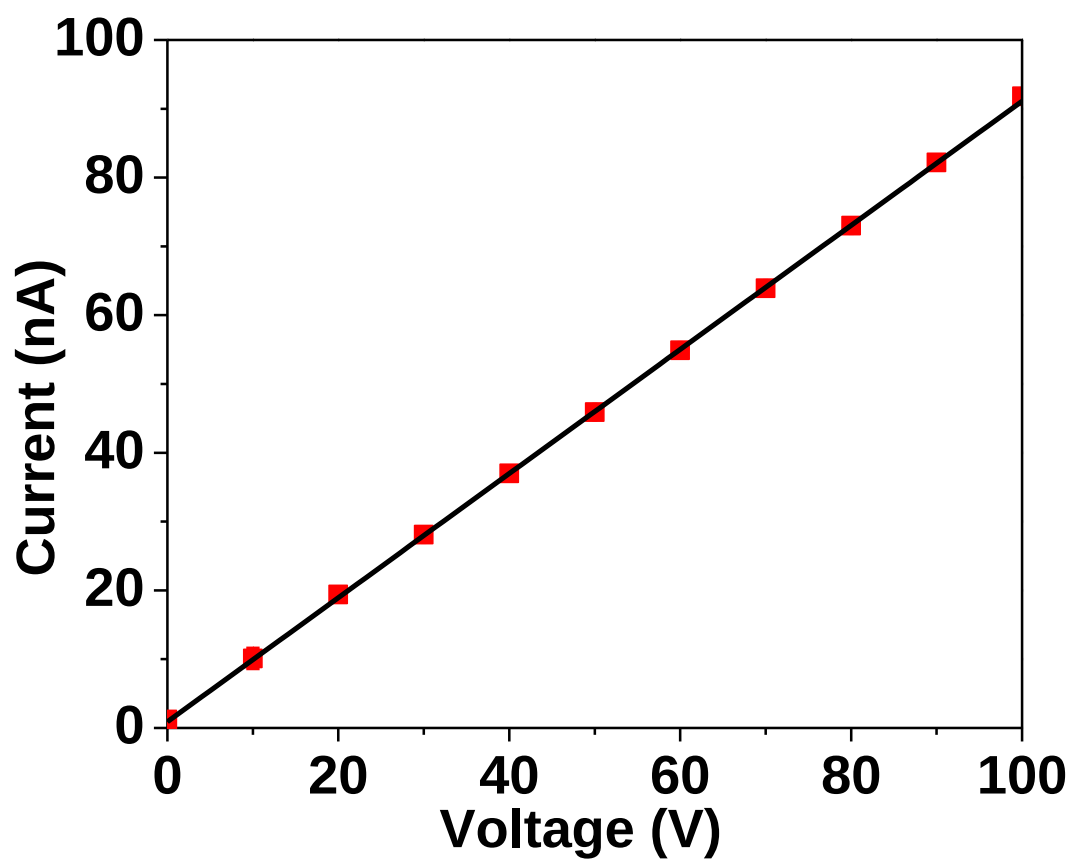


Figure 5.3. Current-voltage scan of MAPbBr₃ device shown in Figure 5.2.

5.2 Impact of Electrode Selection on Device Interfaces

A version of this section was previously published by Jeremy T. Tisdale, Eric Muckley, Mahshid Ahmadi, Travis Smith, Cody Seal, Eric Lukosi, Ilia N. Ivanov, and Bin Hu:⁹³

Tisdale, J. T.; Muckley, E.; Ahmadi, M.; Smith, T.; Seal, C.; Lukosi, E.; Ivanov, I. N.; Hu, B., Dynamic Impact of Electrode Materials on Interface of Single-Crystalline Methylammonium Lead Bromide Perovskite. *Advanced Materials Interfaces* **2018**, 5 (18), 1800476.

Jeremy T. Tisdale conducted all the experiment, characterization, and data analysis and wrote the manuscript. Eric Muckley and Ilia N. Ivanov helped during measurements at the Center for Nanophase Materials Science (CNMS) at Oak Ridge National Laboratory (ORNL). Mahshid Ahmadi, Travis Smith, Cody Seal, Eric Lukosi and Bin Hu helped properly revise the manuscript. Bin Hu and Mahshid Ahmadi helped understand the relevant fundamental mechanisms. The manuscript has been slightly modified for the purpose of this dissertation.

5.2.1. Abstract

One of the current challenges in methylammonium lead halide (MAPbX₃) perovskite application research is understanding contact formation and interfacial phenomena for highly-efficient and stable device performance. For semiconductors, development of contact formation is inseparable from device performance and stability. Single crystalline

MAPbX₃ has become of great interest for perovskite devices in photodetectors, light-emitting diodes and more recently in high-energy radiation detection. Deeper research is required to understand interfacial interactions in single crystalline MAPbX₃. This article focuses on the dynamic impact of electrode metal (Au and Cr) on methylammonium lead bromide (MAPbBr₃) single crystals. We study how charge transport properties of single crystal MAPbBr₃ can be tuned via electrode material selection at the metal/MAPbBr₃ interface to improve device performance with proper contact formation. We demonstrate the ability to create an ohmic-like or non-ohmic contact by switching the electrode metal from Cr to Au, respectively. We observe that the interfacial charge transfer resistance (recombination resistance) of the Cr/MAPbBr₃ interface is $1.79 \times 10^9 \Omega$, compared to $1.32 \times 10^7 \Omega$ for the Au/MAPbBr₃. Cr contacts can reduce hysteretic behavior by reducing interfacial recombination and interfacial polarization. These studies provide insight to metal/MAPbX₃ interfacial interactions towards device engineering for HTL-free MAPbX₃ device structures.

5.2.2. Introduction

Methylammonium lead halide perovskites (MAPbX₃) have been vastly studied for a variety of applications including photovoltaics,⁹⁴⁻⁹⁷ light-emitting diodes,⁹⁸ photodetectors,¹² lasing⁹⁹ and recently for high energy radiation sensors.¹⁰⁰ These materials have gained much interest due to their tunable optical band gaps, desirable electronic properties and low cost.^{28, 101-102} Single crystalline methylammonium lead halide has gained a lot of attention due to its low trap state density, higher mobility and long carrier diffusion length in comparison to thin film MAPbX₃.^{48, 63} In addition, single crystalline MAPbBr₃ is grown

using simple, low-temperature, solution based crystal growth techniques, with the growth process only taking hours to days to complete. For device fabrication, MAPbBr₃ single crystals are easily processed as they grow cubic in shape with parallel sides without the need of complicated control methods during the growth.^{50-51, 103} These factors have made single crystalline MAPbBr₃ a promising material for use in the new generation of low cost electronic devices.

One large focus is on interface engineering via the choice of electrode materials, interfacial layers between the material and electrode and post growth processing before electrode deposition. Many interfacial layers and electrodes have been investigated in thin films for a variety of active materials.¹⁰⁴⁻¹⁰⁸ Extensive research has been concluded on the impact of electrode material selection and interfacial engineering on the electronic properties of MAPbX₃ thin film devices.¹⁰⁹⁻¹¹¹ The typical device structure for MAPbX₃ consists of an anode, an electron transport layer (ETL), the perovskite active layer, a hole transport layer (HTL) and a high work function cathode (e.g., silver, gold, chromium, etc.).¹¹² Although this device structure is commonly used for applications, a well-known alternative uses a HTL-free device structure. These HTL-free devices have been shown to reach high photovoltaic efficiencies,⁹¹⁻⁹² and have been used for the newly discovered application in high-energy radiation detection.^{20, 22} Without the use of HTLs, it is important to understand how different metal electrodes can interact with MAPbX₃ through interfacial interactions. It has been found that the dominant process for charge transport properties and recombination in MAPbX₃ is fast vacancy-mediated anion diffusion.¹¹³ Recently, there has been a great focus on research to understand how different interfaces between MAPbX₃

and single-material contact electrodes affect the charge transport and recombination properties via ion migration.¹¹⁴⁻¹¹⁵ There has been a great effort to study interfacial effects in thin film MAPbX₃ devices. There is a need for research in contact engineering and interfacial phenomena for single crystalline MAPbX₃ devices with advantages such as the absence of grain boundaries and non-crystalline domains, towards deeper understanding of intrinsic properties and improvement of device performance for MAPbX₃-based devices and materials.

Here, we investigate the effects of the interface between single-metal electrodes and single crystalline MAPbBr₃. The metal/semiconductor interfacial interactions are important to understand as HTL-free devices have been gaining attention due to exceptional hole transport properties of MAPbX₃. Because of this, device production is simplified for HTL-free devices without the necessity of deposition of interfacial layers between the active layer and electrode. Ag and Au are among the most commonly used electrodes in MAPbX₃ opto-electronic devices, and in recent literature, Cr electrodes have been used in high-energy radiation detectors based on single crystalline MAPbBr₃. Silver was not chosen due to known chemical reactions that occur when in direct contact with MAPbX₃.¹¹⁶ Therefore, Cr and Au were chosen as model systems to study the impact of metal electrode selection on the electronic properties of single crystalline MAPbBr₃ via interfacial interactions in dark condition, to exclude complexity of photoexcitation during analysis. Also, applications, such as high-energy radiation detection, perform under dark conditions. Cr and Au have work functions of 4.5 eV and 5.1-5.47 eV, respectively.¹¹⁷ Cr has been used for single crystalline MAPbBr₃ device fabrication, which resulted in linear IV response.

On the other hand, Au has been shown to create interfacial polarization with different materials including organic semiconductors and methylammonium lead halide perovskites.¹¹⁸ Here, an in-plane electrode design is used to reduce bulk interactions and directly study the interface between MAPbBr₃ single crystals and the singular metal contact. Also, by using the capacitor-like metal/MAPbBr₃/metal device structure on one surface, we avoid any potential affects from ETLs in a typical device design. This allows us to explore direct correlation between charge transport properties and the interfacial phenomena in the MAPbBr₃/metal contact for development of single-crystalline HTL-free device structures.

5.2.3. Experimental Procedures

Growth of MAPbBr₃

Methylammonium lead bromide (MAPbBr₃) single crystals were grown using the inverse temperature method.⁵⁰ To prepare the growth solution, methylammonium bromide and lead(II) bromide (PbBr₂) were mixed with equimolar amounts in N,N-dimethylformamide (DMF). The solution was constantly stirred for one hour at room temperature. After completely dissolving, the solution was then filtered using a 0.2 µm PTFE filter. After filtration, the solution was divided among vials in 2 mL quantities. The vials were then placed in an oil bath and grown overnight at 75 °C. After growth, the samples were washed using dichloromethane (DCM). All materials used in the growth process were purchased from Sigma-Aldrich and used as received.

Electrode Deposition

Thermal evaporation was used for electrode deposition of Cr and Au. Each electrode was deposited with a thickness of 60 nm using an in-plane electrode design. The in-plane electrode design was chosen to reduce the bulk interactions to study the surface and interfacial effects.

Measurements Techniques

All measurements completed in this article were completed in dark ambient conditions due to the high sensitivity of MAPbBr₃ to light. Tungsten probe tips were used to contact the sample for each measurement in the same arrangement. IV measurements were completed using a Keithley voltage source from -20 to +20 V at a rate of 0.25 V/s. IV hysteresis was measured with the same setup, using LabView to program the scans at different scan rates (0.5, 5 and 50 V/s). For both samples, impedance was measured from 1 Hz to 6 MHz with 0 VDC bias and 1 VAC excitation. EIS Spectrum Analyser was used for modeling impedance traces. The pulsed voltage measurements were conducted using a pulse generator to create a 130 Hz 5 V square wave. The bias was applied to one contact, then the output voltage was measured at the other contact with an oscilloscope in series to study the voltage drop across the device. Photoluminescence was completed with a 405 nm CW laser for photoexcitation.

5.2.4. Results and Discussion

Figures 5.4a and 5.4b show the X-ray diffraction and photoluminescence data for single crystalline MAPbBr₃ studied in this manuscript. The peaks observed in XRD data, and the

PL peak at 536 nm agrees with previous literature and shows that the material studied is single crystalline MAPbBr₃.⁵⁰ Figure 5.4c shows the device structure schematic for the samples. For this device structure, a 5 × 5 × 2 mm crystal was studied as-grown. Two contacts were thermally evaporated on the flat surface of the crystal with a thickness of 60 nm. These contacts were deposited with a width of 1 mm between them with electrode sizes of 4 mm long and 1.5 mm wide. Figures 5.5a and 5.5b show the IV curves for MAPbBr₃ with Cr and Au contacts, respectively. As shown in Figure 5.5a, an ohmic-like contact is formed at the Cr/MAPbBr₃ interface, while a non-ohmic contact is formed at the Au/MAPbBr₃ interface. (Here, we define the ohmic-like behavior as linear dark current in both positive and negative bias directions. The non-ohmic behavior is defined as dark current with exponential behavior. The non-ohmic IV characteristic in MAPbBr₃ single crystals with Au contacts was also reported in earlier studies.¹¹⁹ These characteristics are reproducible across several single crystal devices with Cr and Au contact materials in ambient conditions. Generally, the interface between a semiconductor and electrode materials facilitate the charge transport by providing an energetic offset between the conduction bands. The band gap of MAPbBr₃ is ~2.3 eV, with the conduction band at -4.2 eV and the valence band at -6.5 eV.¹²⁰ The ohmic-like and non-ohmic contact formation in Cr and Au, respectively, can be attributed to the band alignment between the Cr and Au contacts and MAPbBr₃. There is a small potential barrier of around 0.3 eV between the conduction band of MAPbBr₃ and the work function of Cr. Therefore, the small band offset does not limit the current flow through the device, shown of around 0.3 eV between the conduction band of MAPbBr₃ and the work function of Cr.

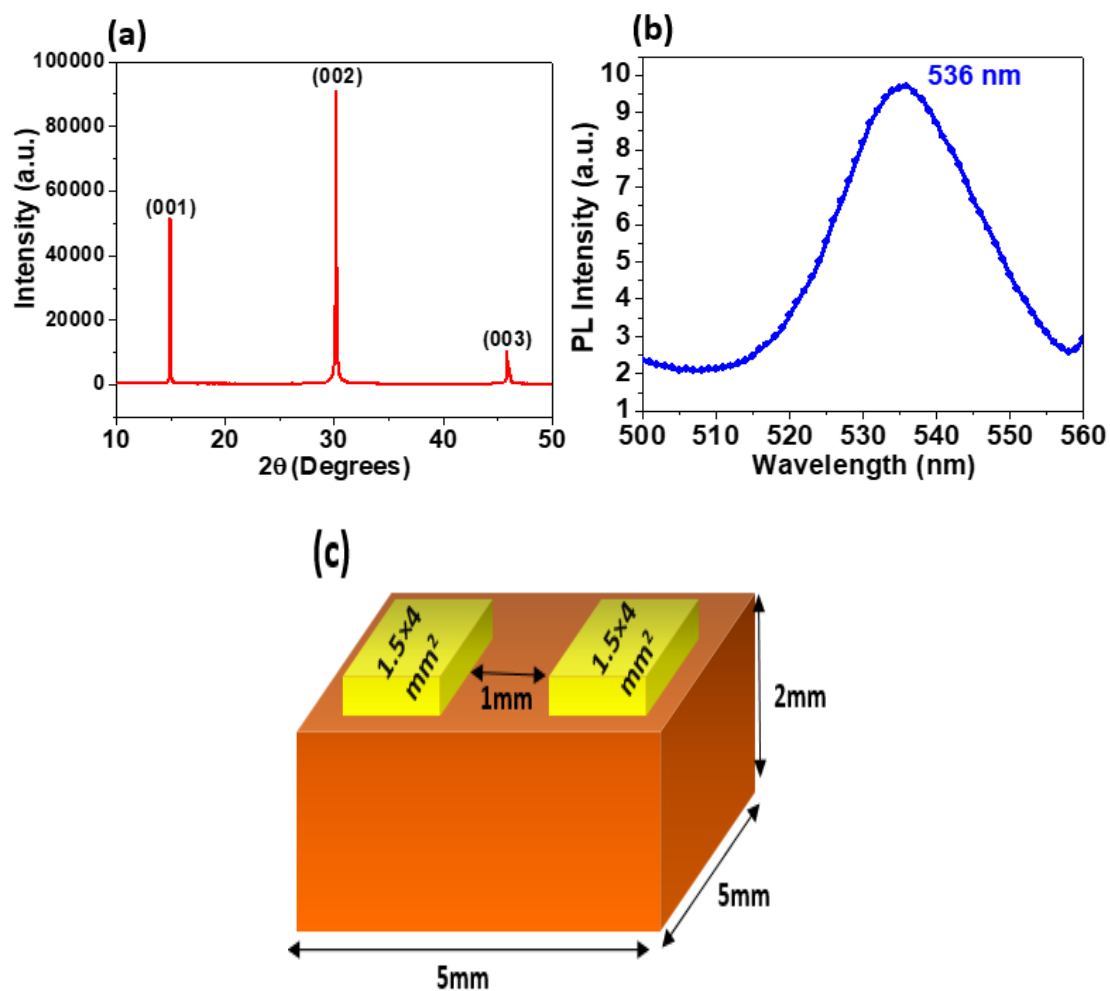


Figure 5.4. (a) XRD for single crystal MAPbBr₃. (b) PL for MAPbBr₃ single crystal (photoexcitation = 405 nm CW laser). (c) Schematic of device architecture used throughout manuscript.

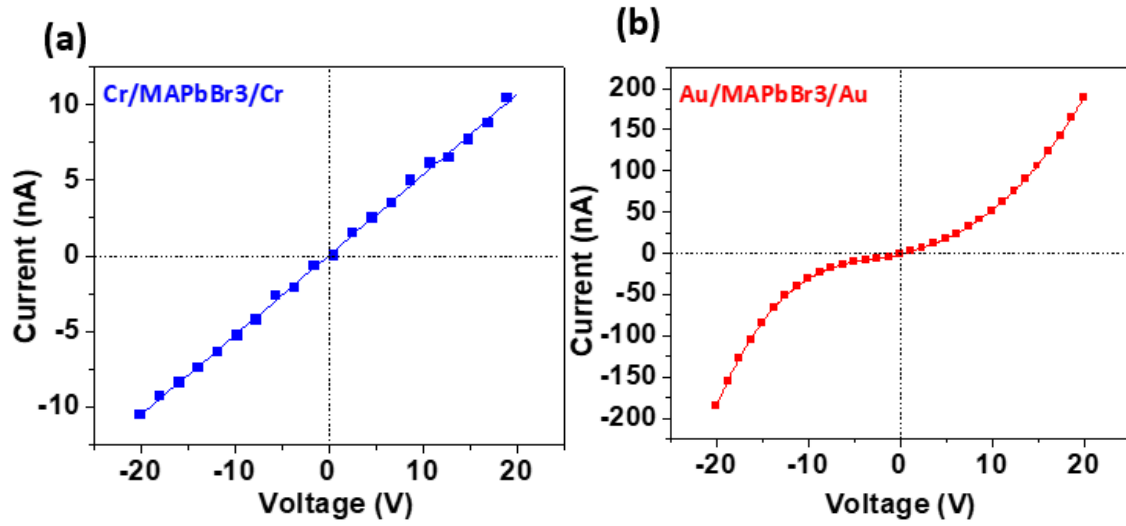


Figure 5.5. IV curves for single crystalline MAPbBr₃ with lateral design device architecture using (a) Cr/Cr contacts and (b) Au/Au contacts.

Therefore, the small band offset does not limit the current flow through the device, shown by the linear increase and decrease with voltage. On the other hand, considering the work function of Au (5.1-5.47 eV), the potential barrier between MAPbBr₃ and Au is much larger (around 0.9-1.37 eV). Because of this larger potential barrier, charge carriers require more energy to move from the single crystal to Au and the non-ohmic behavior is observed with Au contacts.¹²¹ In addition, Au has previously been shown to migrate through MAPbX₃ materials under illumination and heat, severely affecting the performance of devices under working conditions.¹²²⁻¹²⁴ Therefore, control over contact formation and contact phenomena is inseparable from improvement in perovskite device performance and stability. For MAPbX₃ devices, ohmic and non-ohmic contacts can be useful for many diverse applications. Ohmic contacts are desirable for applications such as LEDs (better charge injection) and high-energy radiation detection (better charge collection), whereas non-ohmic contacts are more common for applications such as solar cells. Next, we explored the hysteretic behavior of each device with current-voltage (IV) characteristics, as shown in Figure 5.6. Figure 5.6a shows IV sweeps at different scan rates for the Cr sample. A small amount of hysteresis is observed the device with Cr contacts. Figures 5.6b and 5.6c show hysteresis behavior with the Au contacts. The hysteresis increases significantly in the sample with Au contacts. The hysteresis significantly increases as scan rate decreases from 50 V/s to 0.5 V/s, and it is also time dependent through multiple scans, as seen in Figure 5.6b and 5.6c, respectively. Minimizing hysteresis has been one of the main challenges towards the development of device performance and stability.^{92, 125} Comparing Cr and Au contacts via IV sweeps,

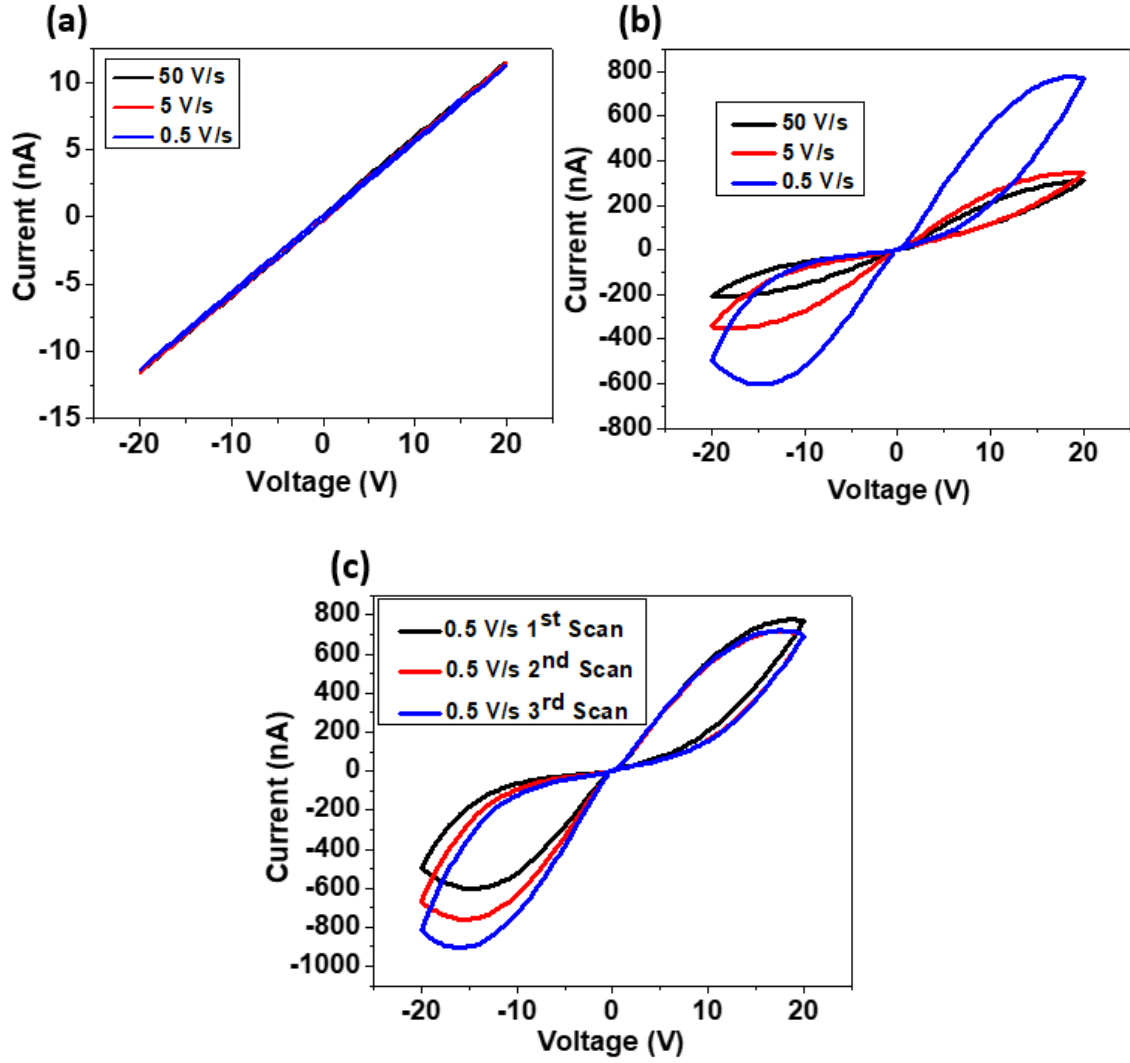


Figure 5.6. IV sweeps for single crystalline MAPbBr₃ with in-plane design device architecture using (a) Cr/Cr contacts (different scan speeds), (b) Au/Au contacts (different scan speeds) and (c) Au/Au Contacts (same scan speeds, multiple scans).

we observe the Cr/MAPbBr₃ interface greatly reduces hysteresis effects as compared to the Au/MAPbBr₃ interface. Several factors can influence hysteresis behavior in MAPbX₃ devices including vacancy-mediated halide migration, interfacial recombination, band alignment and trap states.¹²⁶⁻¹²⁷ Ion migration in MAPbX₃ is discussed in detail by Frost and Walsh, showing that halide migration in MAPbX₃ active layers and interfacial recombination are the dominant mechanisms attributing to device hysteresis.¹¹³ Therefore, we propose that greater hysteresis observed with Au contacts is attributed to two factors: (1) interfacial recombination is greater at the Au/MAPbBr₃ interface and (2) the Au/MAPbBr₃ interface increases the contribution of Br⁻ migration to the electronic properties of MAPbBr₃ and an increase in interfacial recombination compared to the Cr/MAPbBr₃ interface. To gain a deeper understanding about the dynamic processes at the interface between MAPbBr₃ single crystals and metal electrodes, impedance spectroscopy was performed for samples with different metal electrodes (Figure 5.7a and 5.7b). At the mid to high frequency, we are comparing the bulk properties away from the interface. At low frequency, we examine the interface directly.¹²⁸ Low frequency impedance measured on Au electrodes exhibits inductive behavior (Figure 5.7b). This behavior was observed previously for single crystalline MAPbBr₃ and is believed to arise from electronic carrier injection from Au into the perovskite material.¹¹⁹ Inductive effects at MAPbBr₃/Au interfaces will be more thoroughly explored in follow-up experiments. In this study, we used a simplified RC circuit, shown in the inset of Figure 5.7a, to make a direct comparison between the two samples at the metal/MAPbBr₃ interfaces. This equivalent circuit is adapted from previous literature on interfacial properties of MAPbI₃

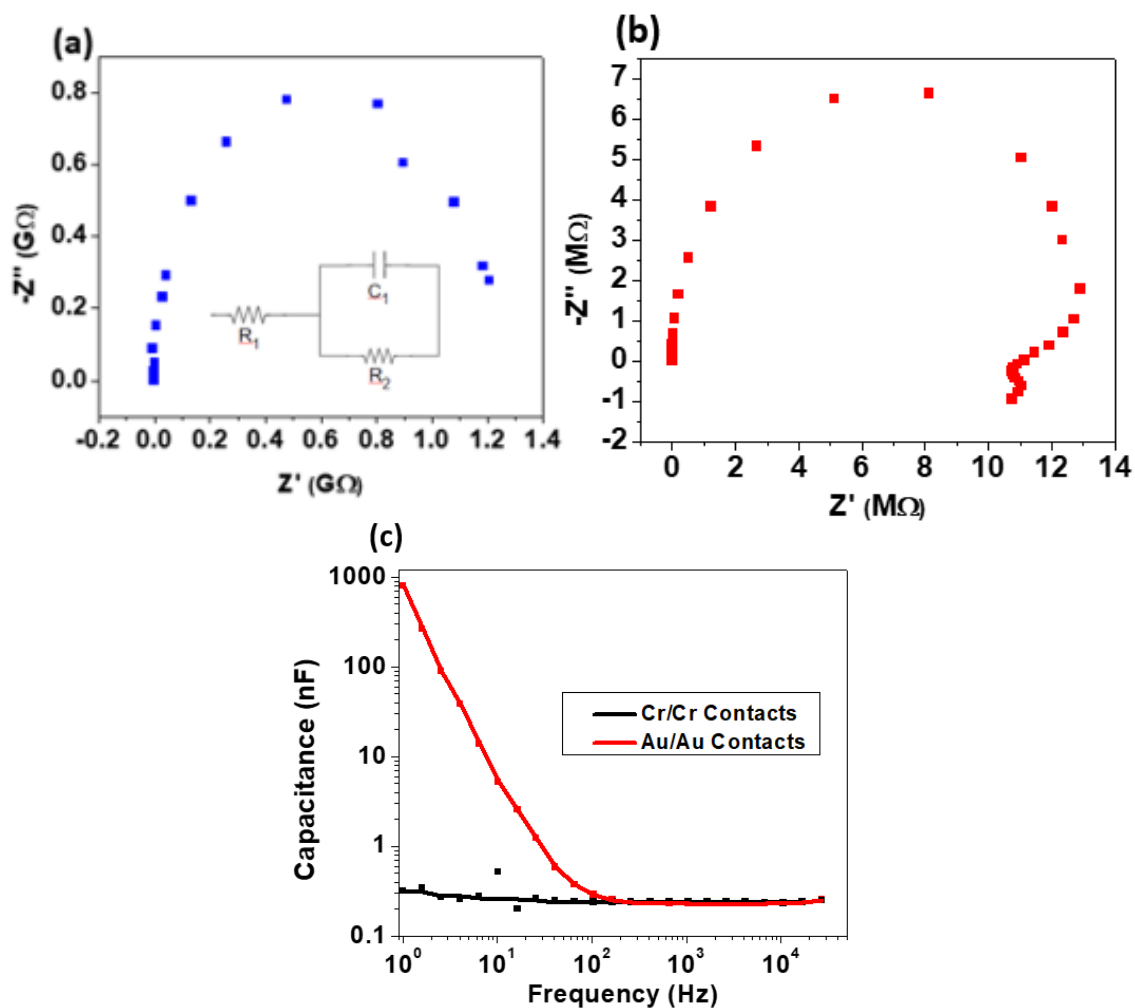


Figure 5.7. Nyquist plots and modeling for single crystalline MAPbBr₃ with lateral design device architecture using (a) Cr/Cr contacts and (b) Au/Au contacts. (c) Capacitance as a function of frequency from impedance spectroscopy.

thin films studied via impedance spectroscopy.¹²⁹ Using this equivalent circuit as representation of the device, we correspond the R1 to the series resistance, as the resistance of Cr and Au are negligible to the overall device. Then, we correspond the R2 and C1 values to the metal/MAPbBr₃ interface. In this perspective, the RC equivalent circuit focuses on differences in the resistive and capacitive nature of the Cr/MAPbBr₃ and Au/MAPbBr₃ interfaces.

Table 5-1 shows the data calculated by the modeling of the two impedance spectra from Figure 5.7. In both samples, R1 is shown to be very close to zero, confirming good contact formation with negligible resistance. Above frequencies of 100 Hz, the capacitance for both devices is shown to be very similar, on the order of 10⁻¹⁰ F. However, the large difference is shown in resistance at R2. The Cr device has a larger resistance of 1.79 GΩ, while the Au device shows a decrease in resistance to 13.2 MΩ. Based on these values, the RC-time constants (τ) were calculated for each device. The Cr device shows a relatively long RC time constant, $\tau = 0.5997$ s. This shows the behavior of the Cr sample is heavily influenced by the high recombination resistance of the Cr/MAPbBr₃. This is also observed by the dark IV characteristics, where the Cr contacts show a much lower dark current, as compared to the Au contacts. (Figure 5.5) The Au has a much shorter RC time constant, $\tau = 0.003$ s, possibly due to the capacitive nature of the Au/MAPbBr₃ at low frequency, observed in Figure 5.7c. Increasing the interfacial charge transfer resistance has been shown to reduce the electron recombination at the interface to enhance photovoltaic properties of MAPbI₃ devices.¹²⁹ Similarly, we expect that increasing the resistance of the MAPbBr₃/metal interface by using Cr over Au will reduce recombination at the interface

Table 5-1. Resistance and capacitance values for two different samples based on a simple RC circuit modeling from high to mid frequency values.

Equivalent Circuit Component	Cr/Cr Contacts	Au/Au Contacts
R₁ (Ohms)	1.08×10^{-8}	8.42×10^{-10}
R₂ (Ohms)	1.79×10^9	1.32×10^7
C₁ (F)	3.35×10^{-10}	2.28×10^{-10}
RC-τ (s)	0.5997	0.0030

and improve charge collection efficiencies in MAPbX₃ devices. Figure 5.7c shows the frequency-dependent capacitance of both samples with Cr and Au contacts. Below 100 Hz, the interfaces of the samples are examined. The sample with Cr contacts shows a very small increase in capacitance from 0.23 nF to 0.31 nF from 100 Hz to 1 Hz. Meanwhile, the sample with Au contacts has a capacitance increase by a factor of $\sim 10^4$ going from 0.3 nF to 1 μ F from 100 to 1 Hz. The increase in capacitance at low frequency gives direct evidence to compare interfacial polarization at the metal/MAPbBr₃ interfaces. The larger capacitance at MAPbBr₃/Au interface clearly shows larger accumulation of both electronic and ionic charge carriers which was previously revealed as the mechanism behind IV hysteresis in perovskite devices.¹¹³ We further explored transient response of the crystals using Cr and Au contacts, as shown in Figure 5.8. In this measurement, a voltage power supply was connected to one contact to bias the device with a 5-volt pulse. Then, the device was connected to an oscilloscope to measure the output of the device (Figure 5.8a inset). In this way, we examine the voltage drop across the device, where a smaller output voltage indicates a larger voltage drop. Because the only variability in the experiments is the electrode metal, (Cr or Au) the differences examined between the two devices directly corresponds to the changes in interactions at the metal/MAPbBr₃ interface. In Figure 5a and 5b, the voltage pulse is represented by the left-hand y-axis, and the voltage output of the device is represented by the right-hand y-axis. First, the rise and decay times of the voltage through the device were compared when the square pulse was turned on and off. In Figure 5.8a, the Cr device shows a rapid response with the square pulse turning on and off. On the other hand, in Figure 5.8b, the Au device shows a slow rise and decay

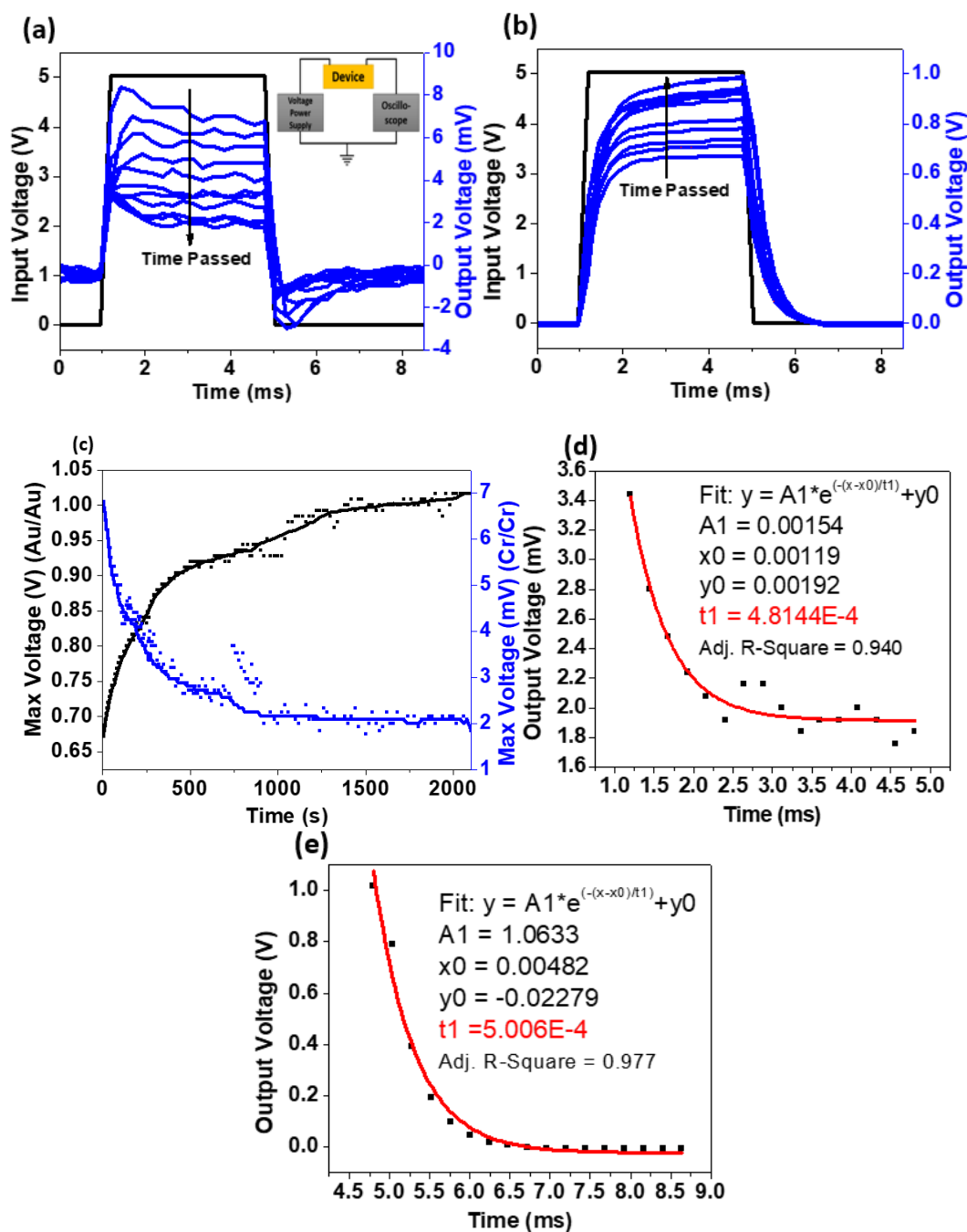


Figure 5.8. Pulse voltage measurements with a 5-volt square wave input for MAPbBr₃ (a) Cr/Cr (0-1500 s) and (b) Au/Au contacts (0-1500 s). (c) Max voltage as a function of time for both samples. (Max voltage is considered the voltage at 5 milliseconds) (d,e) Decay relaxation fit for Cr/Cr and Au/Au contacts, respectively. (5c time scale shows the evolution of pulse voltages for full 35 minutes. 5a and 5b only show 1500 seconds to avoid cluttering of data.)

time in response to the square pulse. Jacobs, et. al. describe how slow transient responses are attributed to both charge trapping and ion migration in MAPbI₃.¹³⁰ When the voltage is turned off for the Cr samples, the output voltage becomes negative for a short time before relaxing back to zero. This relaxation was fitted as shown in Figure 5.8d, showing a relaxation time of 0.48 milliseconds. The fast response to voltage pulses can be attributed to the Cr/MAPbBr₃ interface, where the contact is ohmic and current flow is only restricted by the internal resistance of the device. In addition, because the interfacial resistance is high at the Cr/MAPbBr₃ interface, interfacial recombination and charge trapping are minimized, resulting in the fast response to the voltage pulses. In figure 5.8c, it is shown that this process enhances the resistance of the device as the output voltage decreases over time under repetitive pulsed voltages. It is a small decrease of ~5 mV after 2000 s of repetitive voltage pulsing. The increase in resistance can be explained by charge/ion redistribution to an equilibrium state after 1000 s of voltage pulses, as the change in output voltage significantly decreases at this time. The Au contacts show a slow rise (when voltage is on) and decay (when voltage is off). The relaxation here was fitted in Figure 5.8e, giving a relaxation time of 0.5 milliseconds. In Figure 5.8c, it is shown that this process reduces the resistance of the device as the output voltage increases over time under repetitive pulse voltages. Because the Au/MAPbBr₃ interface was shown to have relatively high interfacial polarization from impedance spectroscopy, we attribute the slow response of the output voltage to high interfacial polarization due to ion migration and accumulation of charges, as well as charge trapping at the interface. Therefore, we show that ion migration has a large impact on the electronic properties at the Au/MAPbBr₃ interface, as compared to the

Cr/MAPbBr₃ interface. It was previously shown in thin film perovskite devices with inverted structure that the accumulation of ions at the perovskite/electrode interface results in decreasing the Schottky barrier height, resulting in an increase in interfacial resistance.¹³¹ This is confirmed here by the increasing output voltage through time (Figure 5.8c). Combining this information with hysteresis, we show that hysteresis can be heavily reduced from MAPbX₃-based opto-electronic devices by choosing the correct electrode metal with high interfacial resistance and low interfacial polarization. The ion redistribution and ion migration proposed here are both shown to be reversible processes as the hysteresis in both contact schemes returns to the starting current position at zero voltage. Further investigation would be required for full device structures under working conditions to better understand the reversibility or irreversibility of these processes at metal/MAPbBr₃ interfaces, as well as further exploration on the influence of chemical interactions on I-V and impedance characteristics at the metal-MAPbX₃ interfaces.

5.2.5. Conclusions

In summary, we investigated the effects of electrode material on the electrical properties in single crystalline MAPbBr₃ devices. We found that Cr contacts greatly reduce the amount of hysteresis at the metal/MAPbBr₃ interface, compared to the large hysteresis observed with Au contacts. We show that the Cr contacts increase the interfacial resistance of the sample by over a factor of 100, which reduces the amount of interfacial recombination. We also observed that Au creates a much stronger interfacial polarization leading to increased contribution of Br⁻ migration to the electronic properties. In this way, we conclude that using Cr electrodes at a direct Cr/MAPbBr₃ interface greatly reduces

hysteresis effects via combined properties of weak interfacial polarization to reduce contribution of ion migration in MAPbBr₃ and stronger interfacial resistance to reduce interfacial recombination forming an ohmic-like contact, whereas the Au/MAPbBr₃ interface forms a non-ohmic contact. We believe this work provides deeper understanding on ion migration and recombination properties at interfaces and emphasizes the significant impact of interfacial effects at metal/MAPbBr₃ on electronic properties of MAPbBr₃ single crystalline devices towards future application research using HTL-free device structures.

6 Application Results

In this chapter, results from application measurements will be reported. Radiation detection and photodetection will be the focus for experimental measurements discussed in this chapter. Radiation measurements included in this chapter were done in collaboration with Travis Smith and Prof. Eric Lukosi in the Nuclear Engineering department at the University of Tennessee, Knoxville. Jeremy T. Tisdale has written all explanations and analysis of the data within this dissertation.

6.1 Photodetection

A photodetector, or photosensor, is an optoelectronic device that absorbs photons of light to create e-h pairs and measures the photo-response in current collected from the electron and hole charge transfer to respective electrodes, as previously shown in Figure 2.5, in section 2.2. Figure 6.1a shows a schematic representation of an in-plane MAPbBr₃ photodetector. This device consists of one Ag electrode and one Au electrode to create a built-in electric field through the device to promote proper charge transfer. The electrodes were separated by a distance of 1 mm. The energy diagram, shown in Figure 6.1b, shows the work functions of Ag and Au with respect to the band structure of the MAPbBr₃ single crystal active layer. The work function of Ag is -4.7 eV is close to the CB of MAPbBr₃, which prefers the flow of electrons. Meanwhile, the work function of Au is 5.1 eV. Although this work function is not as close to the VB of MAPbBr₃, it is closer than the Ag electrode. Therefore, the Au prefers the flow of holes. The holes have a much higher energy barrier at the interface (1.1 eV) than the electrons have at the Ag interface (0.2 eV), which can have adverse effects on the interfacial recombination, lowering photodetection properties of the device, depending on which electrode is the source and

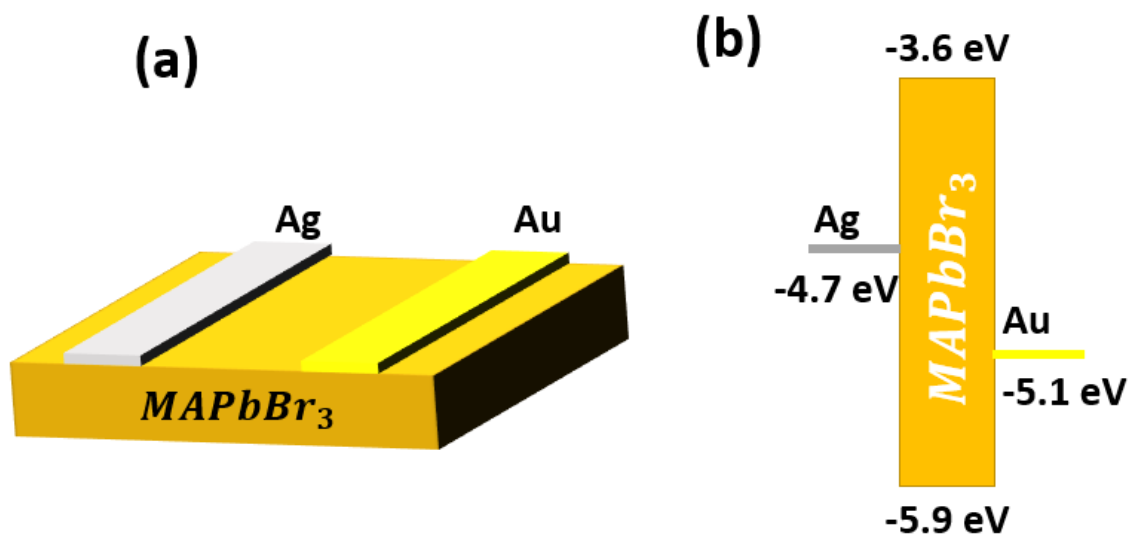


Figure 6.1. Photodetection device structure shown (a) schematically for the in-plane structure and (b) energy diagram for electrodes and MAPbBr₃.

which electrode is the drain. The built-in electric field through the device allows for a “self-powered” non-biased photodetector, which has been previously reported for perovskite-based photodetectors.¹³² Typically, a small bias of ~ 1 V is used during operation of photodetectors to further promote charge transfer processes. Figure 6.2 shows the photodynamic response of the device schematically shown in Figure 6.1. Figure 6.2a shows the photo-response of the device when the Au contact is the source electrode and the Ag contact is the drain. Figure 6.2b shows the photo-response of the device when the Ag contact is the source electrode and the Au contact is the drain. Ag was earlier discussed, in section 5.2, to make a poor direct contact with MAPbBr₃ due to chemical reactions at the interface of Ag and OMHPs forming Ag-halide components.¹¹⁶ However, for this experimental data, Ag was used as a low work function electrode, close to the CB of MAPbBr₃ for a low energy barrier, and measurements were made immediately after thermal evaporation of Ag to avoid contribution of the chemical interactions. After the devices were stored under vacuum, in a desiccator, for three days, the appearance of Ag was no longer shiny and no longer made consistent contact at the electrode. Therefore, the Ag interactions with MAPbBr₃ did not affect the photodetection measurements, as the chemical reaction between the electrode and crystal take longer than the measurements taken after the first three to four hours after device fabrication.

Photocurrent measurements were made by first supplying a 1 V bias to the device from the source to the drain of the device. The dark current of the device when the photoexcitation is turned off is $I = 2.4 - 2.5 \times 10^{-8}$ A. This yields a device resistance of $R \approx 4 \times 10^7 \Omega$,

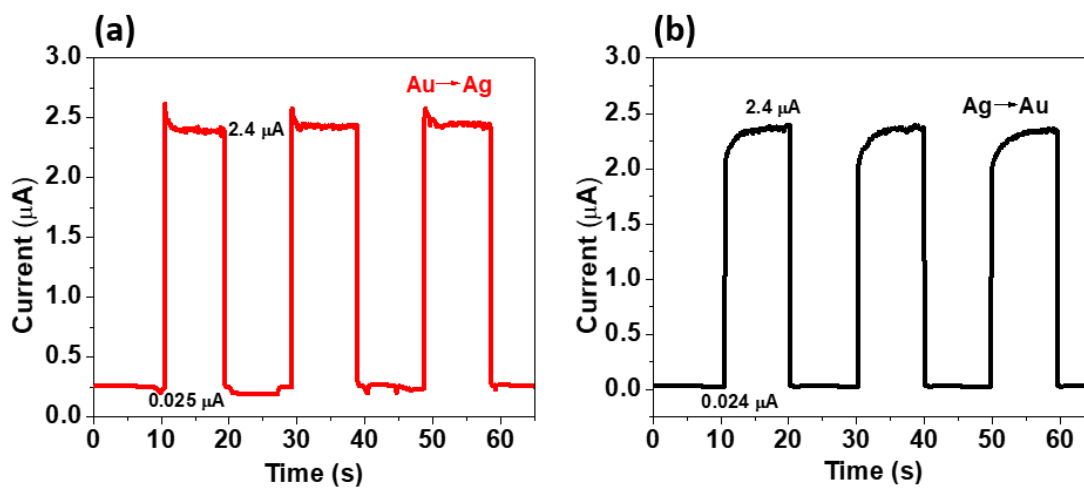


Figure 6.2. Time-dependent photocurrent response (bias = 1 V) of MAPbBr₃ single crystalline device. (a) Device biased with Ag contact as drain. (b) Device Biased from with Au contact as drain.

which agrees with the Au-based device structures reported on in the work presented in section 5.2.⁹³ During the photodynamic measurement, the device was exposed to a solar simulator under 1 sun condition. The frequency of the source was kept very low ($f = 0.05 \text{ Hz}$) to investigate the photoresponsivity and the saturation behavior of the photodetector. In both configurations of the source and drain of the device, there is a large increase/decrease of the photocurrent when the solar simulator is turned on/off. This shows that the MAPbBr₃ device has great photoresponsiveness. Figure 6.2a shows the photo-response (defined as the time it takes the photocurrent to go from 10% to 90% of the device's maximum value) for the in-plane MAPbBr₃ device structure, where the Au contact is the source, and the Ag contact is the drain. The stabilized current under photoexcitation (I_L) for this device is $I_L = 2.5 \times 10^{-6} \text{ A}$. The photosensitivity ($\frac{I_L - I_d}{I_d}$) of the device is 9.99×10^2 .¹³² The rise time response to the photoexcitation is 85 ms and the decay is very similar at 86 ms, showing a fast on and off response to the light, which is desirable for efficient photodetection. With the Ag drain, the energy barrier at the Ag/MAPbBr₃ is very low at 0.2 eV. Because of this, a large amount of photogenerated electron-hole pairs are created immediately, displayed by the initial peak photocurrent at $I_{L,max} = 2.62 \times 10^{-6} \text{ A}$, which is 0.12 μA more than the stabilized photocurrent. After a short time, (ms-time scale) the photocurrent decreases to a stabilized value of 2.5 μA (decrease of 4.58%). This decrease (seen in every cycle) is due to a combination of quick photogeneration of charge and charge recombination in the MAPbBr₃. The decay after the initial response shows that although the photogenerated electron-hole pairs migrate along the electric field through the device immediately, charge recombination also occurs on a

similar time scale. Once the photogeneration of charges and charge recombination reach a dynamic equilibrium, the photocurrent reaches its stable value.¹³³ Another reason for the decrease in photocurrent after the initial response relies on photoinduced bulk polarization and lattice distortion. When electron-hole pairs are generated in the CB and VB of the material, the material becomes electronically polarized.¹³⁴ MAPbBr₃ is known to be a highly polar crystal, which causes electron-phonon coupling due to localization of electronic carriers.¹³⁵ This causes lattice distortion, which increases the resistance of the crystal, causing the gradual decrease in photocurrent under illumination.

Figure 6.2b shows the photodynamic response of the device when the Au contact is the drain. Here, the energy barrier at the Au/MAPbBr₃ interface (1.1 eV) is much larger than the Ag/MAPbBr₃ interface. The photosensitivity of the device in this direction is similar to the other direction at 9.59×10^2 . However, the large interfacial energy barrier prompts different photodynamic behavior in the device. First, the on/off response of the device is much slower in this direction with a rise time of 245 ms and a decay time of 170 ms. Also, opposite to the curve shape of the Ag interface, when the photocurrent first responds, the initial photocurrent is lower and gradually increases. This is due to the large energy barrier at the Au/MAPbBr₃. Because of this barrier, charge accumulation easily occurs at the interface, which increases the probability of interfacial recombination. These results agree with the interfacial work previously discussed in section 5.2.⁹³ These results provide valuable insight towards charge transfer and charge recombination processes inside of OMHP optoelectronic devices and other sensing devices, where charge transfer and charge recombination are shown to be competing processes on a similar time scale. The MAPbBr₃

shows excellent photoresponsivity with quick on/off response, desirable for all sensing applications. The comparison between Au and Ag electrodes also shows the importance of proper band alignment in OMHP based devices, which drastically affected the response time and response behavior in the MAPbBr₃ in-plane photodetector.

6.2 High-Energy Radiation Detection

The main goal of this work is to develop OMHP single crystalline material for high-energy radiation detection. Here, experimental results on MAPbBr₃-based devices is investigated. The device structure used for all radiation measurements is the out-of-plane device structure shown in Figure 5.2 (HTL-free, out-of-plane, device structure consisting of Cr/BCP/C₆₀/MAPbBr₃/Cr). A typical set-up for testing semiconducting radiation detectors is schematically shown in Figure 6.3. When an incident photon from high-energy radiation interacts with the semiconductor detector, an electron is ionized. This ionized electron generates e-h pairs, which are recorded as charge as the e-h pairs dissociate and move through the detector. This low amplitude signal is processed by a charge sensitive preamplifier, which transforms the peak to a pulse that shows the rise time and decay time of the associated charge. This signal is passed through a shaping amplifier to process the pulse into a Gaussian shape with peak amplitude equivalent to the energy deposited by the incident radiation photon. Once the pulse is shaped into a Gaussian curve, the signal passes through a peak sensing analog to digital converter (ADC). One particular ADC used is a multichannel analyzer (MCA). The MCA is used to digitize the analog signal from the shaping amplifier. The MCA analyzes each pulse individually and stores the information of each pulse. The pulse amplitude (pulse height) for each pulse is recorded and binned

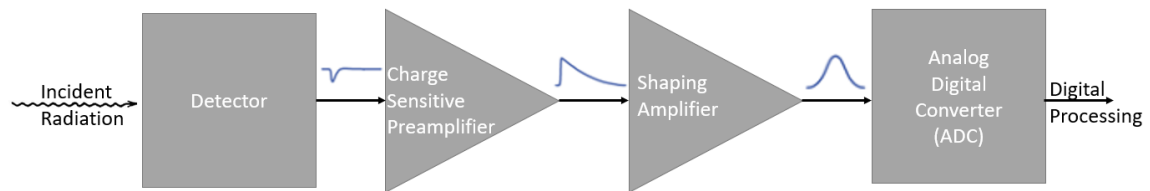


Figure 6.3. Block diagram of pulse processing chain for pulse processing of radiation detection signal.

from 0 to 10 V. The accuracy and amount of pulse heights differentiated between depends on the number of channels used for the MCA. By doing so, the MCA passes this information to digital processing software that plots a histogram of the frequency against pulse height of all the pulses recorded in a period of time. This type of MCA processing can be used to analyze energy distributions inside the detector from incident radiation photons. The setup shown in Figure 6.3 was used to characterize the radiation responsivity of MAPbBr₃-based devices in the following experiments.

The first radiation experiments completed involved the detection of charged alpha particles. Alpha particles are high energy radiation photons that have a short range. Therefore, these particles deposit all of their energy in the near-surface region of the absorber material. Because of this deposition of energy, the balance of charge carriers does not heavily affect the signal processing. In this perspective, the MAPbBr₃-based detectors can be measured by the hole transport, ignoring the lesser electron transport. Figure 6.4 schematically shows how the α -particles deposit their energy on the detector. ²¹⁰Po decays with 100% probability of alpha particles, which have an energy of 5.304 MeV. Alpha particles have a very short range in air of 2 to 10 cm. Because of this, alpha particles are easily attenuated by any solid medium, and deposit all of their energy in the near-surface region of the detector. Here, the alpha particles interact with the MAPbBr₃ by ionizing the atoms in the material, i.e. removing the electrons from the outer shell of the atoms. When the atoms are ionized, electron-hole pairs are formed at the cathode surface, and the electrons and holes separate and transfer to the cathode and anode, respectively. Because the alpha particles deposit all of their energy at the near-surface region, only one charge

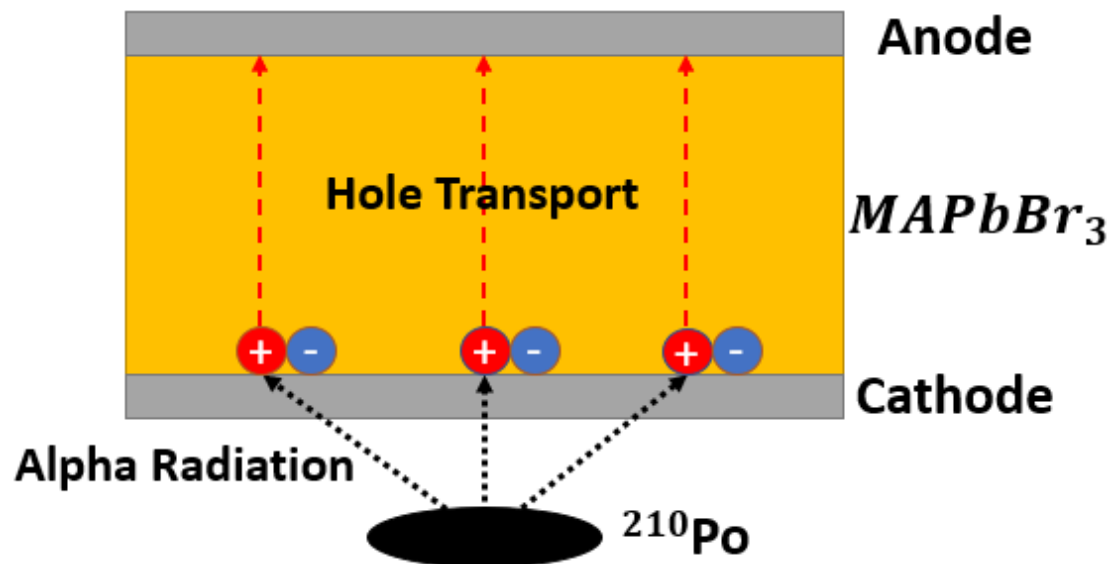


Figure 6.4. Principle of interactions and radiation sensing for α -particles in the MAPbBr_3 detector.

carrier is collected for charge collection. The charge carrier desired is controlled by the face of the detector that is exposed to alpha particles and the bias of the opposite electrode. In the case of MAPbBr₃, which is a p-type material, holes are the majority charge carrier. Therefore, the cathode surface is exposed to the alpha radiation, and the cathode is biased with a negative voltage to collect holes. Because the electron-hole pairs are generated at the surface near the cathode, the holes transfer through the bulk of the material, generating a larger signal of charge. On the other hand, the electrons travel a very short distance to the cathode, which results in a low signal.

Figure 6.5 shows radiation sensing of ²¹⁰Po alpha particles using the device structure shown in Figure 5.2a at different bias voltages for a MAPbBr₃-based detector. The alpha radiation was exposed to the cathode-side of the detector, and the anode was negatively biased for the collection of holes, as depicted in Figure 6.4. The detector was biased at a range of biases including -25 V, -50 V, -70 V, -100 V, and -120 V. Each spectrum was collected for 120 seconds, except the -50 V bias run, which was run for 300 seconds. In each plot, the noise floor was removed from each curve to compare the radiation peaks. Data collected from the different biases are tabulated in Table 6-1. The charge carrier velocity is dependent on the charge carrier mobility (intrinsic to the material) and the electric field, which is a function of detector bias. Therefore, it is shown in Figure 6.5a-e, that the peak position of response increases with the increase of bias voltage. This shows that the signal processed by the electronic is true response to the exposure of alpha particles, as the charge carrier velocity increases with electric field. As the bias voltage increases, the drift velocity of the charge carriers saturates. Plotting the peak position in channel number as a function

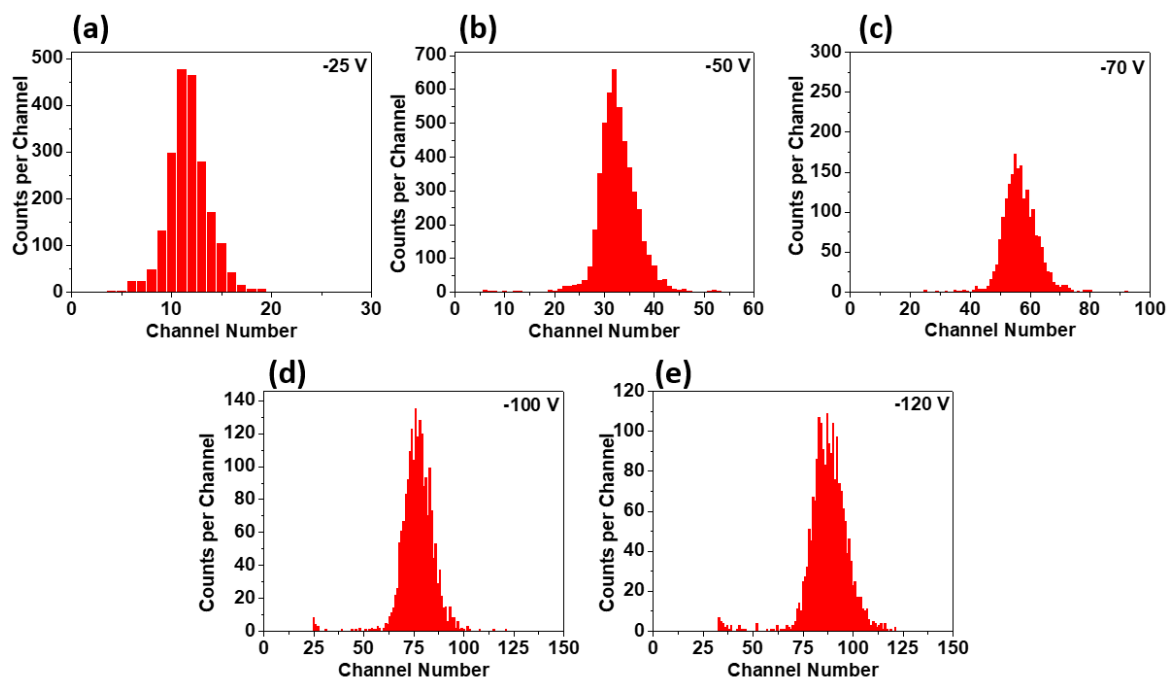


Figure 6.5. Alpha radiation response from ^{210}Po alpha source of a MAPbBr_3 single crystalline-based detector biased at (a) -25 V, (b) -50 V, (c) -70 V, (d) -100 V, and (e) -120 V.

Table 6-1. Important parameters from alpha radiation detection of MAPbBr₃ detectors shown in Figure 6.5.

Bias (V)	Peak Position (Channel #)	FWHM (Channel #)	CPS	Resolution (%)
-25	11.55	3.94	17.44	34.11
-50	32.30	7.28	16.28	22.54
-70	56.16	11.32	16.15	20.16
-100	76.85	14.84	16.76	19.31
-120	87.54	17.84	16.61	20.38

of bias voltage allows fitting by the Hecht equation, shown by Equation 6.1,

$$Q(V) = \frac{N_0 q V (\mu\tau)}{d^2} \left(1 - \exp \left(-\frac{d^2}{(\mu\tau)V} \right) \right) \quad (6.1)$$

where N_0 is the number of charge carriers generated by incident radiation, Q is the total charge collected, d is the thickness of the detector, q is electronic charge, V is the applied bias voltage, μ is the charge carrier mobility, and τ is the charge carrier lifetime. Solving this equation for the $\mu\tau$ -product for a single charge carrier is an essential defining parameter for radiation sensors. The devices prepared in this work have been characterized in this way to produce a $\mu\tau$ -product for holes at $3.40 \pm 0.18 \times 10^{-4} \text{ cm}^2/\text{V}$.¹³⁶ This value is in agreement with previous reported values for MAPbBr₃-based detectors.²⁰ As shown in Figure 6.5 and Table 6-1, the peak position is proportional to the increase in bias voltage as expected. Also, as bias increases the separation from the noise floor increases, which is essential for detection of lower energy incident radiation. The detector resolution, calculated by dividing the FWHM by the peak position, stays consistent around 20% once the detector is biased at -50 V or higher. Finally, the counts per second (CPS) of the measured spectra is also consistent at an average of 16.65 ± 0.23 . All of the data recorded in Table 6-1, and the consistency between values at different biases, verifies the response to alpha radiation for the MAPbBr₃-based detector.

Other than detection of charged particles, MAPbBr₃ has shown promising initial results for dual gamma/neutron response, as shown in Figure 6.6. Dual gamma/neutron sensing is made possible by the inorganic/organic hybrid nature of MAPbBr₃. Gamma photons can interact with the absorber material due to heavy-Z Pb present in the crystal structure. Simultaneously, neutrons can interact with the hydrogen in the crystal. This gives the

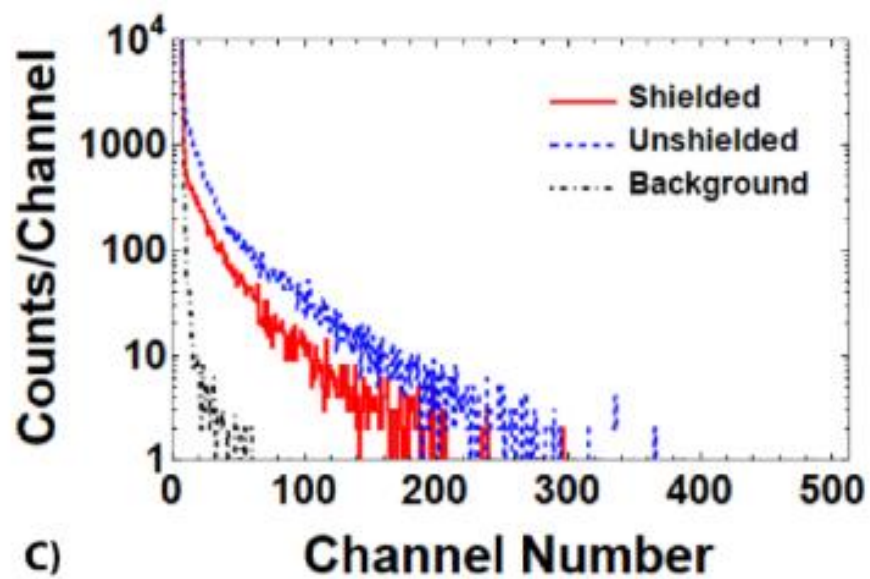


Figure 6.6. Neutron/gamma sensing from a shielded/unshielded $^{239}\text{Pu}/\text{Be}$ source for MAPbBr_3 detector.¹³⁶

material a unique property to simultaneously sense gamma photon and neutrons. To experimentally show the capability of dual detection, the MAPbBr₃ detector was exposed to a ²³¹Pu/Be source, which gives off gamma photons and neutrons. The background signal (with no source present) is compared to the signal with full exposure to the unshielded ²³¹Pu/Be source. It is clear here that charge is generated by the exposure to the radiation. Then, the detector was shielded from the ²³¹Pu/Be source with six inches of lead. Here, the lead shielding is used to attenuate the gamma photons from the detector, while still allowing the neutrons to interact with the MAPbBr₃. The signal generated when the detector is shielded from gamma photons clearly decreases from the elimination of gamma interactions, yet still clearly shows charge generation due to interactions with neutrons. This experiment shows that MAPbBr₃ possesses a unique property for dual gamma/neutron detection.¹³⁶ Although the MAPbBr₃ detectors show response to gamma photons, a photopeak from gamma sensing has yet to be achieved. This is a goal that is on-going for the duration of the project, and future work on the project will strive to achieve the photopeak based on the initial development of the material outlined here. Because the photopeak from gamma sensing has not been achieved, alpha particles have been mainly used to characterize high-energy radiation detection properties of MAPbBr₃-based Figure 6.7 shows alpha detection responses of low purity and high purity detectors based on the crystals grown and discussed in section 4.2. For these measurements the device structure shown in Figure 5.2a was used. All detectors were biased at -50 V on the Cr anode. Rise time analysis from the preamplifier output pulse is also shown in Figure 6.8, and Table 6-2 provides an analysis of the results from Figures 6.7 and 6.8. First, the high purity detectors

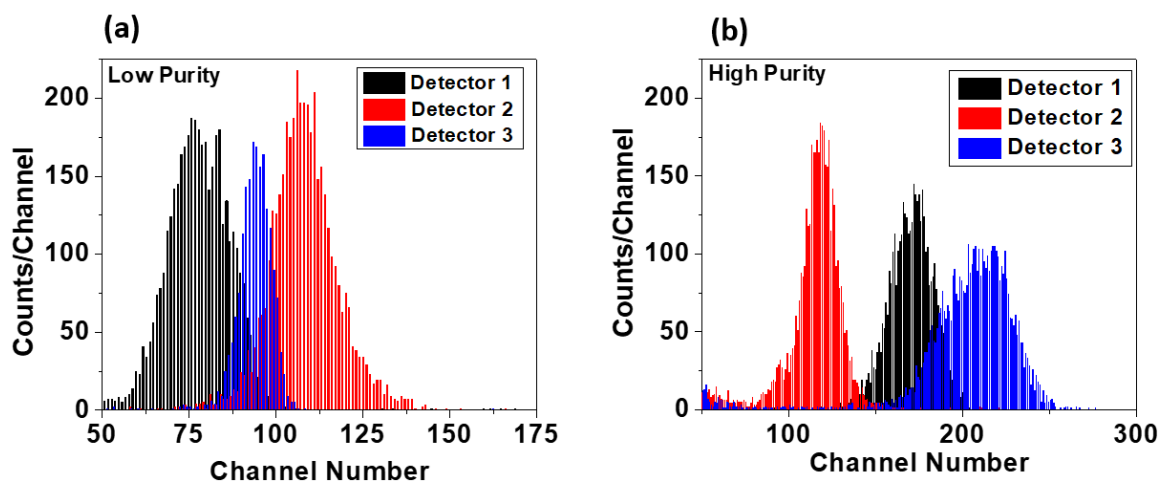


Figure 6.7. ^{210}Po alpha particle spectra collected at a -50 V bias for (a) low purity MAPbBr₃ detector and (b) high purity MAPbBr₃ detector.

present a larger signal amplitude (H_0) than the low purity detectors. The average H_0 for low purity detectors is 92 ± 16 channels, and the average H_0 for high purity detectors is 166 ± 45 channels. This corresponds to an average increase in signal amplitude by $80.44 \pm 12.6\%$. The average energy resolution of the detectors was calculated to be $18.16 \pm 7.25\%$ for the low purity detectors and $18.13 \pm 1.79\%$ for the high purity detectors. Although the average resolution between the low and high purity detectors is very similar, the larger standard deviation in the low purity samples may be attributed to the regions of disordered, nano-sized crystalline domains, causing more microstructural differences between the low purity detectors, whereas the high purity detectors show to have more consistent microstructural features and properties. The increase in signal amplitude alludes to higher CCE in the high purity detectors. However, the larger signal can also arise from an increase in sample mobility. To investigate the hole mobility for each detector, the rise time of the MAPbBr₃ detectors were evaluated on an oscilloscope from the preamplifier traces to determine the charge collection or rise time of charge carriers.¹³⁷⁻¹³⁹ Ballistic deficit was removed from the preamplifier using a cascade of partial deconvolutions.¹⁴⁰ 100 preamplifier traces for each low purity and high purity detector were aligned and averaged. These results are shown in Figure 6.8b. After deconvolution of the preamplifier pulses, the high purity detectors collected an average of $32 \pm 30\%$ more charge than the low purity detectors corresponding to the maximum amplitude observed from the preamplifier traces. Additionally, each of the low purity detectors shows a two-component rise in the pulse

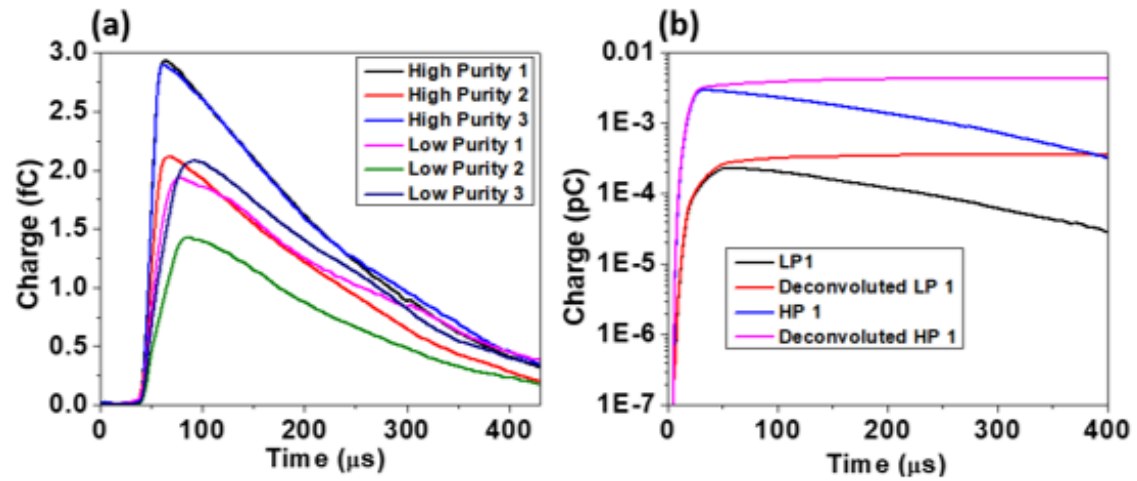


Figure 6.8. Preamplifier output pulse for both (a) low purity and (b) high purity based radiation detectors.

Table 6-2. Rise time and drift mobility ($cm^2/V \cdot s$) estimations and statistical data for low and high purity detectors.

Sample	Thickness (mm)	H ₀ (Channel number)	Resolution (%)	Rise time (μs)	Mobility ($cm^2/V/s$)
LP 1	1.9406 ± 0.0025	77	26.0	17.5 ± 0.7	17.9 ± 0.7
LP 2	2.0853 ± 0.0025	94	11.7	20.5 ± 0.8	17.7 ± 0.7
LP 3	2.0218 ± 0.0025	108	16.7	23.6 ± 0.9	14.4 ± 0.6
HP 1	1.4935 ± 0.0025	118	19.89	10.1 ± 0.4	18.4 ± 0.8
HP 2	1.5951 ± 0.0025	172	16.3	11.3 ± 0.5	18.9 ± 0.8
HP 3	1.3183 ± 0.0025	208	18.3	9.5 ± 0.4	15.3 ± 0.6

signals. After a fast-initial rise, the slope of the rise decreases by about 20 to 25 microseconds. The slower component of the signal rise is attributed to charge trapping and detrapping behavior. The high purity detectors, on the other hand, show a one component rise with a fast rise time to maximum amplitude of each pulse, showing that the same trapping behavior is not prevalent in the rise times of the high purity detectors. In Table 6-2, the drift mobility for each detector is calculated based on the rise time of the detector, the thickness of the detector, and the electric field through the detector. Assuming a flat electric field, the mobility of the detector can be calculated by dividing the drift velocity by the electric field, where the drift velocity is based on the observed rise time from 10% maximum to 90% maximum value of the averaged preamplifier traces. The average hole drift mobility for the low purity detectors was $16.7 \pm 1.9 \text{ cm}^2/\text{V} \cdot \text{s}$, and the average electron drift mobility for the high purity detectors was $17.5 \pm 1.9 \text{ cm}^2/\text{V} \cdot \text{s}$. While the difference in hole mobility between the low and high purity samples helps explain the effect of potential error in evaluating the results if ballistic deficit is not considered, the larger average signal amplitude from the high purity samples clearly indicates that the improvement on microstructural features and crystalline domains results in a reduction of charge trapping/detrapping, which ultimately improves the CCE of the devices. Although the energy resolution of the devices did not increase using high purity precursors, the increase in CCE is an essential parameter towards efficient radiation sensing devices. Maximizing the CCE increase the signal-to-noise ratio and increase the separation of the signal from the noise floor, which enables sensing of lower energy X-rays and gamma rays that would otherwise be covered up by the noise floor in the signals.

Through the work reported on precursor purity, it was shown that using higher purity precursors led to increase CCE towards enhancing the performance of MAPbBr₃-based radiation sensors. However, the problem of imbalanced charge transfer between electrons and holes still exists. Here, MAPbBr₃ crystals were doped with small amounts of Cl⁻ in an attempt to balance the charge transfer properties for MAPbBr_{2.94}Cl_{0.06} single crystals, as discussed in section 4.3. To investigate the possibility of balancing electron and hole charge transport, MAPbBr₃-detectors and MAPbBr_{2.94}Cl_{0.06}-based detectors were exposed to alpha radiation from a ²¹⁰Po source. First, the incident radiation was exposed to the cathode of the detectors, the anode was biased at -50 V, and the alpha spectra was recorded for the signal processed from holes. Then, the incident radiation was exposed to the anode of the detectors, the cathode was biased at +50 V, and the alpha spectra was recorded for the signal processed from electrons. Figure 6.9 shows the spectra collected for each detector type. Figures 6.9a and 6.9c show the spectra via collection of holes for the MAPbBr₃ and the MAPbBr_{2.94}Cl_{0.06} detectors, respectively. The holes signal from the MAPbBr₃-based detector is cleaner than the holes signal from the MAPbBr_{2.94}Cl_{0.06}-based detector. The signal amplitude of the MAPbBr₃-based detector is slightly higher, the signal-to-noise ratio is improved, and the detector resolution is higher. This may be due to lesser stability of the MAPbBr_{2.94}Cl_{0.06}-based detector at constant bias. However, looking at the spectra generated via collection of electrons in Figures 6.9b, and 6.9d, the MAPbBr₃ detector shows no peak for the 5.3 MeV alpha particles. Meanwhile, the MAPbBr_{2.94}Cl_{0.06} detector shows a proper spectrum for the 5.3 MeV alpha particles from ²¹⁰Po. Although the peak is close to the noise floor compared to the signal generated from hole collection, the presence

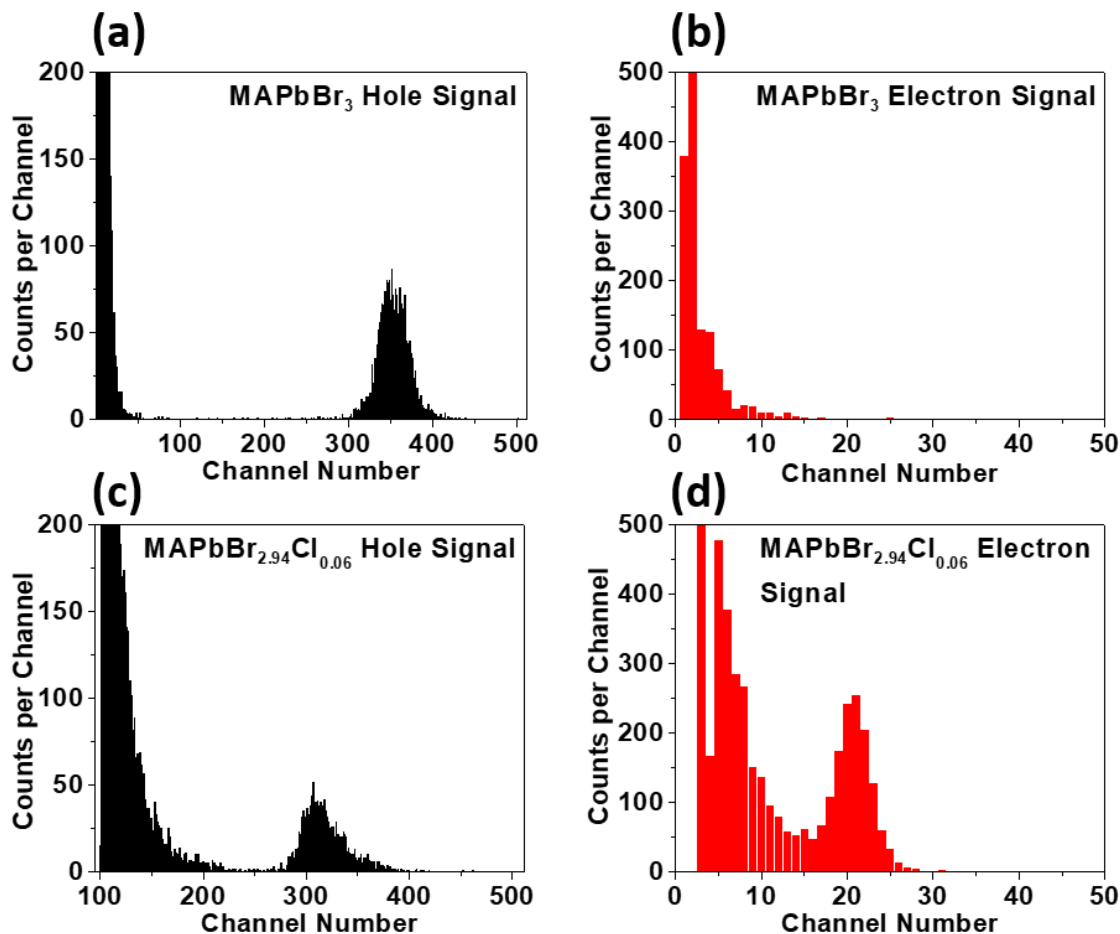


Figure 6.9. Radiation sensing signal from ^{210}Po alpha particles for (a) MAPbBr₃ holes (b) MAPbBr₃ electrons (c) MAPbBr_{2.94}Cl_{0.06} holes and (d) MAPbBr_{2.94}Cl_{0.06} electrons. Each detector biased at 50 V (negative bias for holes and positive bias for electrons).

of the clear alpha peak shows that the electron mobility in the device is indeed enhanced through the partial doping of Cl^- for Br^- . This agrees with previous studies showing that Cl^- substitution in MAPbBr_3 crystals improves the balance of charge carriers towards developing efficient gamma ray sensing.²²

Conclusions

Conclusions made in this work are summarized as follows:

- Cost effective ($< \$10 \text{ cm}^{-3}$), high quality growth of OMHP single crystals has been demonstrated via inverse temperature crystallization growth method, with accurate control over the growth parameters.
- XRD patterns, especially Laue orientation patterns, show that the MAPbBr_3 single crystals grow with perfect orientation in the (100) plane on the top face, and grow in the perfectly orientated (001) direction from perfect orientation on the side planes.
- Using a MABr-rich ratio of precursors in the growth solutions of MAPbBr_3 improves the quality of important properties, such as bulk resistivity, by reducing the amount of defects, due to the differences in solubility between PbBr_2 and MABr in DMF.
- Growth of larger volume crystals can be achieved by using an original MAPbBr_3 as a seed crystal in fresh solution and grown again. This process can be done multiple times to achieve a desired size for the final single crystal.
- Elemental analysis of MAPbBr_3 single crystals grown with low and high purity precursors provides significant insight that impurities in precursors are not incorporated into the crystal structure during the solution-based growth. However, the impurities do act as nucleation sites, changing the μ -scale features of crystalline domains, which have a large effect on charge trapping.
- Successful doping has been demonstrated via substitution of other organic halides, such as MAI for MABr in ITC crystal growth solutions. This provides a simple

doping mechanism towards tuning optical and electrical properties of OMHP single crystals for optoelectronic and sensing applications.

- The use of interfacial layers, such as C₆₀ for an ETL, provides post-growth, device fabrication processes towards enhancing charge transport properties for OMHP-based devices.
- The use of HTL-free device structures brings attention to the choice of electrode material at the metal/semiconductor interface. The importance of proper electrode selection has been shown, where the energy barrier at the interface plays a key role in the charge transport properties at the interface. Au showed to have a negative effect on charge transfer due to the large energy barrier, decreasing the interfacial resistance and showing negative polarization effects. On the other hand, Cr showed to have a positive effect on charge transfer at the interface, due to proper band alignment, to reduce interfacial hysteresis and reduce the probability of interfacial recombination.
- MAPbBr₃-based photodetectors showed great performance with a quick response to photons from low-energy solar simulator, with high photosensitivity (up to 1×10^3), and a high, stable photocurrent.
- Photodetection has also been a useful tool in understanding charge transfer processes in optoelectronic OMHP devices. The photocurrent results presented reveal effects of ion migration, device polarization, and the competition between charge collection and charge recombination.
- Results on the alpha particle detection with MAPbBr₃-based detectors shows that the material is a promising candidate for ionizing radiation detection.

- The use of high purity precursors shows to have a positive effect in increasing the size and reducing the disorder of crystalline domains in the grown MAPbBr₃ single crystals. The use of high purity precursors showed more consistent microstructural features that reduced the amount of charge trapping through the single crystal, thereby increasing the CCE of high purity-based detectors.
- The use of alpha radiation sensing rise time analysis has been demonstrated as a useful tool to discern information about the drift velocity of single charge carriers. In this way, hole and electron mobilities can be calculated separately.
- Quantitative analysis on the MAPbBr₃ detector's figures of merit (such as bulk resistivity, drift mobility, charge carrier lifetimes, $\mu\tau$ -product) have been verified and are in agreeance with previously reported values in literature.
- MAPbBr₃ possesses the capability of dual gamma/neutron sensing due to its hybrid inorganic/organic framework. Pb helps the detection of gamma photons, while the hydrogen content allows the detection of neutrons. MAPbBr₃ dual gamma/neutron has been experimentally demonstrated via sensing of a ²³¹Pu/Be source with and without heavy lead shielding.
- Small amounts of Cl⁻ doping have been shown to allow for moderate resolution gamma sensing. Here, the alpha particle radiation sensing demonstrates the ability to process electrical signal of holes and electrons separately, due to the increased balance of electron and hole transport in the MAPbBr_{2.94}Cl_{0.06} single crystal.

Overall, the importance of developing novel, alternative radiation sensing materials is fully discussed. The need for a lower-cost, easily grown radiation sensing materials is crucial for radiation safety. The initial development of MAPbBr₃-based radiation detectors presented here shows promising results towards efficient high-energy radiation detection. This development is also useful in understanding optoelectronic properties towards other optoelectronic applications.

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Appendix

List of Abbreviations

CZT – CdZnTe - Cadmium Zinc Telluride
HPGe – HyperPure Germanium
OMHP – Organometallic Halide Perovskite
MAPbX₃ – Methylammonium Lead Halide
PCE – Power Conversion Efficiency
LED – Light-Emitting Diode
PL – Photoluminescence
VB – Valence Band
CB – Conduction Band
CCE – Charge Collection Efficiency
PVD – Physical Vapor Deposition
CVD – Chemical Vapor Deposition
TSSG – Top-Seeded Solution Growth
AVC – Anti-solvent Vapor-assisted Crystallization
ITC – Inverse Temperature Crystallization
HI – Hydroiodic Acid
MAX – Methylammonium Halide
DMF – N,N-Dimethylformamide
GBL – γ -butyrolactone
D^{CM} – Dichloromethane
PMT – Photo-multiplier Tube
EQE – External Quantum Efficiency
DMSO – Dimethyl Sulfoxide
C₆₀ – (6,6)-Phenyl C₆₁ Butyric Acid Methyl Ester
IV – Current-Voltage
SCLC – Space-Charge-Limited Current
XRD – X-ray Diffraction
SEM – Scanning Electron Microscopy
EDS – Energy-Dispersive X-Ray Spectroscopy
ToF-SIMS – Time-of-Flight Secondary Ion Mass Spectrometry
EELS – Electron Energy Loss Spectroscopy
CW – Continuous Wavelength
O.D. – Optical Density
eV – Electron Volts
FWHM – Full-Width Half MAX
HRXRD – High Resolution X-Ray Diffraction
EA – Ethylammonium
MA – Methylammonium
HTL – Hole Transport Layer
ASTM – American Society for Testing and Materials
ADC – Analog-to-Digital Converter
CPS – Counts Per Second

Vita

Jeremy T. Tisdale was born in April of 1991. He completed his Bachelor of Science in Materials Science and Engineering at the University of Tennessee – Knoxville in May of 2013. He then continued on for graduate studies in Materials Science and Engineering at the University of Tennessee and achieved his Master of Science under the supervision of Dr. Bin Hu, completing his thesis titled “Study of Magneto-Optical Behaviors at a Ferromagnetic/Organic Semiconductor Interface,” in May of 2016. He then continued pursuing his Ph.D. degree in Materials Science and Engineering, under the supervision of Dr. Bin Hu, starting in August of 2013, in research pertaining to development of hybrid perovskite single crystals.