Efficient Lead-Free Perovskite Solar Cell

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ABSTRACT

Solar energy has made tremendous strides in the past decade. These advances have increased the efficiency, decreased the cost, and increased the reliability of photovoltaic systems[1]. These advances are largely due to the manufacturing process and the ability to produce solar cells more efficiently. However, progress can be made to further advance the economic viability of solar energy. A great contender in advancing photovoltaics are perovskite solar cells.

Perovskite solar cells have increased their efficiency from 3.8% in 2009 to 22.7% in late 2017[2]. Perovskite solar cells have the potential to achieve higher efficiencies at very low production costs. The goal of this project is to design a lead-free perovskite solar cell with an efficiency of 10%. Perovskite research is moving away from away from lead-based materials because lead is less stable and is very toxic. This is important for the economic success and environmental viability of perovskite solar cells.

1. INTRODUCTION AND MOTIVATION

In recent history, the world has become aware of a potential energy crisis. The world's population continues to expand along with the use of technology and the internet. The U.S. Energy Information predicts that the world energy consumption will grow by 28% from 2015 to 2048[3]. To match this increase in consumption the world must produce this energy cleanly to mitigate the damage done by greenhouse gasses. Many climate models predict that the global-average surface warming will increase 1.4-5.6 Celsius by 2100, relative to 1990[4]. This temperature increase is a concern because it could potentially damage many ecosystems, and it could drastically affect how humans interact with their environment.

A sustainable method for achieving this increase in consumption is the implementation of solar energy. The U.S. Department of Energy's (DOE) National Renewable Energy Laboratory (NREL) analysis of solar energy showed that utility-scale solar costs have declined by 30 percent, with residential- and commercial-scale solar prices lagging by 6 and 15 percent reductions, respectively[5]. These cost reductions are due to decreases in PV module and inverter prices, lower labor costs, and higher module efficiency.

Many commercial solar panels on the market are made of multi-crystalline silicon and single-crystalline silicon which accounts for about 94% of the market[6]. The remaining 6% are composed of thin film technologies, such as, cadmium telluride (CdTe) and copper indium gallium selenide (CIGS). *TABLE I* compares the max efficiencies of these solar cells.

TABLE I: Comparison of commercial solar cell record efficiencies as of July 2017[6]

Material	Efficiency
Multi-Crystalline Silicon	26.7%
Single-Crystalline Silicon	21.9%
CdTe	21%
CIGS	21.7%

These cells have gained popularity in the market because they have decent efficiencies and the production costs are low. To keep solar energy competitive with fossil fuels, progress must continue to improve solar cell technology. A potential competitor is the perovskite solar cell because these cells have efficiencies comparable to market technology and their potential to be produced at very low costs. Perovskite solar cell includes a perovskite structured compound, which normally is a hybrid organic-inorganic lead halide-based material as the absorption layer. Perovskite solar cells have gained large popularity among scientists because their efficiency has increased from 3.8% in 2009 to 22.7% in late 2017[2]. This cell is more efficient than both thin-film technologies and the single-crystalline silicon solar cell.

Perovskite solar cell production can easily be scaled up to be market competitors. Researchers can currently deposit these materials using methods like spin coating and blade spreading. These methods could be implemented to mass produce these cells at a very low production cost. They also open the idea of other methods like printing solar cells using an InkJet printer.

Even with recent success, perovskite solar cells still have very large obstacles that limit the potential this technology has in commercial markets. This includes their toxicity, stability, and hysteretic current voltage behavior. This paper will focus on toxicity and stability, but the problem of hysteretic current voltage behavior could be a result of low stability and should be researched more in the future.

Many high efficiency (~20%) perovskite solar cells are made with lead; the toxicity of the cell is very high. This high toxicity prevents these cells from being implemented into the market because of the potential of introducing large amounts of lead into the environment when these solar cells are operating or when they are eventually retired and recycled.

Lead-based perovskite solar cells also have very short life times because of issues with their stability. The factors that affect device stability are moisture, ultraviolet (UV) light, and temperature[7]. Which are very common factors for the environment that many solar cells operate in. To make these cells a market competitor, these problems must be solved.

The issues of toxicity and stability could be solved by producing lead-free perovskite solar cells. Researches at Brown University and University of Nebraska - Lincoln (UNL) believe that lead-free perovskite solar cells could increase stability, while eliminating the need for toxic materials like lead. Their research group constructed a thin-film perovskite solar cell using a titanium-based material. This cell had an efficiency of 3.3%, which is low compared to lead-based alternatives[8]. However, this cell had an open-circuit voltage above one volt, which is larger than other lead-free alternatives. These lead-free alternatives use materials like tin, titanium, and bismuth which are abundant materials in the world. This will drive the cost of lead-free perovskites down because they will not require the rare earth materials used in many other solar cell technologies.

To advance the development of lead-free perovskite solar cells, this project will first develop a lead-base perovskite solar cell baseline within the Crosslight TCAD software. Then other lead-free alternatives will be explored using various compounds in simulation with a goal of 10% efficiency in the

best material. The performance of these devices will be compared to a lead-based perovskite solar cell bassline to better understand these devices and to evaluate if lead-free perovskite solar cells can compete with their lead-based counter parts.

2. TECHNICAL BACKGROUND

Perovskite solar cells are a type of solar cell with an absorption layer consisting of a hybrid organic-inorganic halide-base material. When this material has a perovskite structure it is termed a perovskite solar cell. Generally, a perovskite is anything with a ABX_3 form and the same structure as the perovskite mineral. The perovskite lattice arrangement and other perovskite derivatives are shown below in *FIGURE 1*.

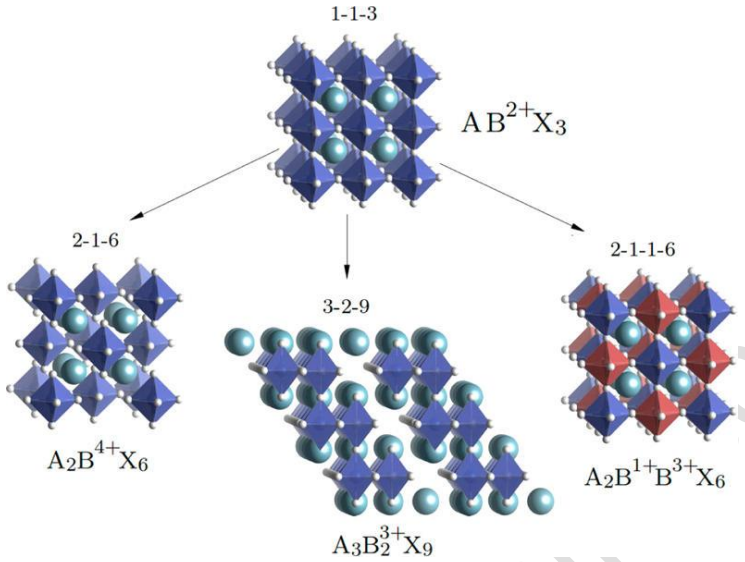


FIGURE 1: Schematic of basic perovskite structure and its lead-free perovskite derivatives[9].

In *FIGURE 1* the letters A, B, and X are:

- A = An organic cation
- B = An inorganic cation
- X = A halogen anion

This helps understand why perovskites are called a hybrid organic-inorganic halide-based material. Some examples of possible materials are shown below in *TABLE 2*.

TABLE II: Possible Materials used in Perovskites[9]

A	B	C
Methylammonium (CH_3NH_3)	Pb	I
Formamidinum (H_2NCHNH_2)	Sn	Br
Cs	Ti	Cl
$CH(CH_3)$	BiAg	-

This table shows only a small sample of the potential materials that could be used. The choice of each material is crucial for determining characteristics such as bandgap, absorption coefficient, diffusion lengths, carrier masses and carrier mobility.

Perovskite solar cells are in their own category because of their crystal structure, but their operation is similar to other thin-film solar cells. Perovskite solar cell operates by the photovoltaic effect where a

photon excites an electron into the conduction band. The perovskite solar cell structure is a diode junction, this means an electric field is generated at the junction interface. This electric field sweeps the excited carriers to the opposite contact generating photocurrent. This generated current follows the ideal diode equation (*EQUATION 1)*.

$$J(V) = J_{SC} - J_0(e^{\frac{qV}{k_B T}} - 1) \qquad \textit{EQUATION 1}$$

Where J_{SC}, is the short-circuit current density of the cell, J_0, is the dark current, V, is the applied voltage, k_B, is the Boltzmann constant, and T, is the temperature of the cell.

When a solar cell is illuminated, and the voltage is swept a current density versus voltage plot can be generated. From this curve solar cell performance parameters can be extracted. This curve provides scientists with short-circuit density, open-circuit voltage (V_{OC}), maximum power point (P_{MAX} at V_M and I_M), fill factor (*FF*), and efficiency (n). The fill factor is calculated using *EQUATION 2*.

$$FF = \frac{V_M I_M}{V_{OC} I_{SC}} \qquad \textit{EQUATION 2}$$

The efficiency of the solar cell is calculated using *EQUATION 3*.

$$n = \frac{P_{MAX}}{P_{IN}} = \frac{V_M I_M}{P_{IN}} \qquad \textit{EQUATION 3}$$

Where P_{IN}, is the incident power on the solar cell. An example curve of a solar cell is shown below in *FIGURE 2*.

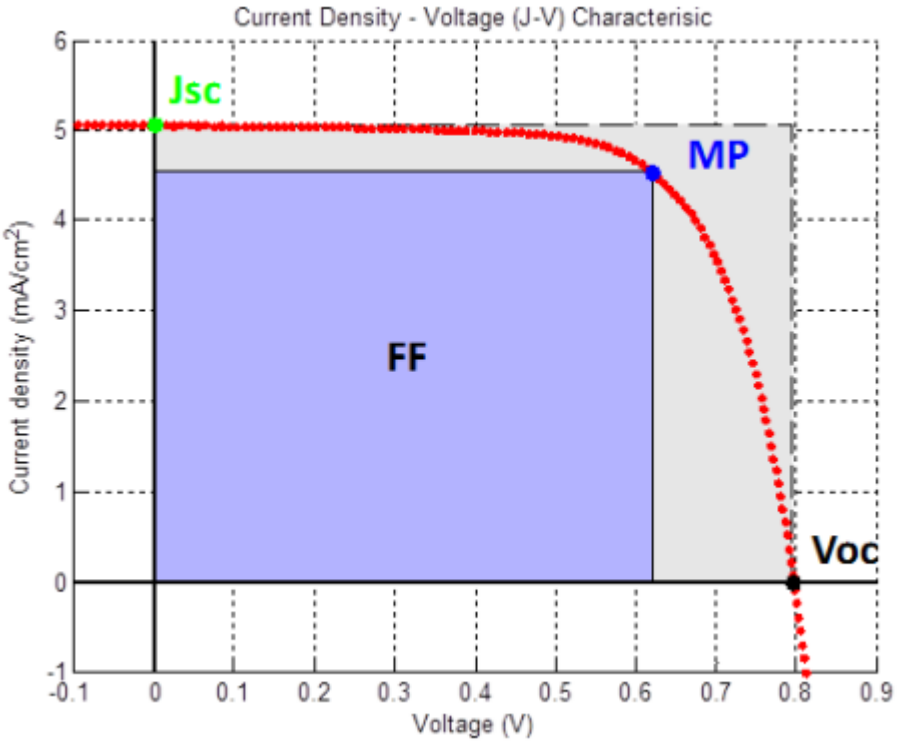


FIGURE 2: An example of current density versus voltage curve of a solar cell. The J_{SC}, V_{OC}, and P_{MAX} are shown. The ratio of the blue area and the gray area is the fill factor of the solar cell[10].

3. DEVICE STURCTURE, DESIGN, AND SIMULATION RESULTS

To investigate the performance of various lead-free perovskite solar cells, simulations were performed in Crosslight TCAD software. The Crosslight software did not contain the material files required to simulate perovskite solar cells. The paper by Minemoto and Murata stated that device modeling of perovskite-based solar cells could be performed using the CIGS material mentioned in the previous section. Perovskite solar cells employ a similar structure with inorganic semiconductor solar cells like CIGS[11]. This is done because perovskite solar cells are a very new technology and there is no detailed report on device modeling of perovskite solar cells. The main difference between organic and inorganic absorbers is the exciton type. The exciton in the perovskite material is typical Wannier-type exciton, making it similar to the inorganic CIGS absorber[12]. The fact that the exciton type and structural similarity between CIGS and perovskites are the same allow for device modeling.

The paper by Minemoto and Murata was seeking to simulate a perovskite solar cell with a Methylammonium Lead-base absorber ($CH_3NH_3PbI_{3-x}Cl_x$) and compare it with the real device to test the validity of the device modeling. *FIGURE 3* shows the device structure of the perovskite solar cell from their simulation. The solar cell consists of transparent conductive oxide (TCO)/buffer/absorber/hole transport material (HTM). These are based on SnO_2:F (FTO), TiO_2, $CH_3NH_3PbI_{3-x}Cl_x$, and 2,2',7,7'-tetrakis(N,N-p-dimethoxy-phenylamino)-9,9'-siprobifluorene (Spiro-OMeTAD), respectively. *TABLE III* summarizes the device parameters for their simulation[11].

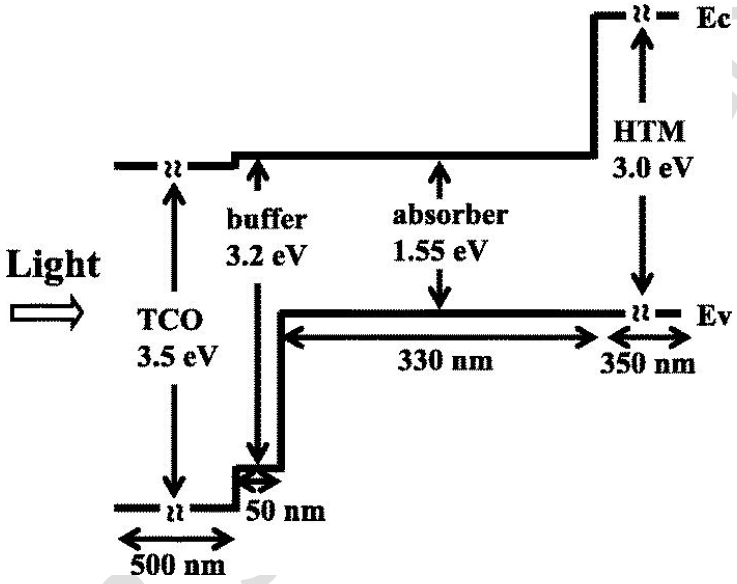


FIGURE 3: Device structure used in paper simulation[11].

TABLE III: Simulation parameters of perovskite solar cell in the study by Minemoto and Murata[11]

Parameters	SnO_2:F (TCO)	TiO_2 (buffer)	IDL1 (defect layer)	$CH_3NH_3PbI_{3-x}Cl_x$ (absorber)	IDL2 (defect layer)	Spiro-OMeTAD (HTM)
Thickness (nm)	500	50	10	350	10	350
N_A (cm^{-3})	-	-	-	-	-	$2x10^{18}$
N_D (cm^{-3})	$2x10^{19}$	10^{16}	10^{13}	10^{13}	10^{13}	-
ε_r	9.0	9.0	6.5	6.5	6.5	3.0
X (eV) (Affinity)	4.0	3.9	3.9	3.9	3.9	2.45
E_g (eV)	3.5	3.2	1.55	1.55	1.55	3.0

$\frac{\mu_n}{\mu_p}(\frac{cm^2}{Vs})$	20/10	20/10	2.0/2.0	2.0/2.0	2.0/2.0	$2x10^{-4}/2x10^{-4}$
N_t (cm^{-3})	10^{15}	10^{15}	10^{17}	$2.5x10^{13}$	10^{17}	10^{15}

Where IDL1 and IDL2 are defect layers to consider the interface recombination between their respective layers. The results from Minemoto and Murata's simulation is shown below in *FIGURE 4*.

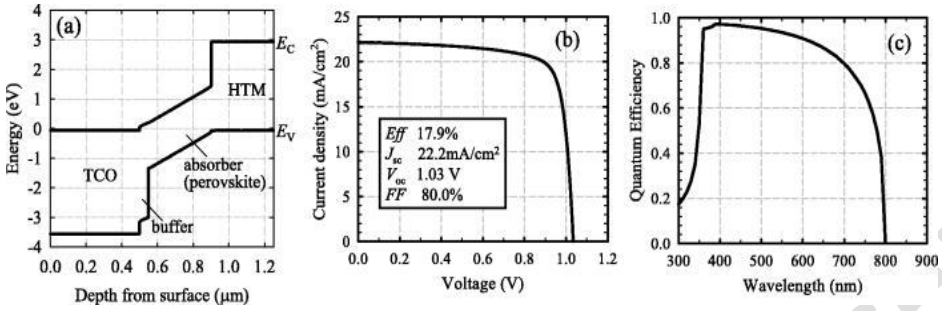


FIGURE 4: (a) Energy band diagram, (b) J-V curve, and (c) QE characteristics[11].

These results confirmed that perovskite solar cell could be simulated using CIGS material to reflect a real device.

Now that it is know that CIGS can be used to simulate perovskite solar cells, the first step of this project was to reproduce these results in the Crosslight software to achieve a baseline for a lead-based solar cell. In addition to not having perovskite solar cell materials, the Crosslight software was also missing the TCO and HTM layers of the device. The TCO layer, SnO_2:F, was replaced with ZnO_2 because it was considered a TCO within the Crosslight material files. The material files were updated with the information contained within *TABLE III* to reflect SnO_2:F. The HTM layer, Spiro-OMeTAD, was replaced with gold (Au) because it has been used directly following the HTM layer in other research papers[13]. The material files were updated to treat Au as a semiconductor with properties from *TABLE III* to reflect Spiro-OMeTAD. The last change made within the Crosslight software was changing the TiO_2 material parameters. This was done because originally in Crosslight, TiO_2 is treated as an insulator instead of a semiconductor. The parameters were also updated to reflect *TABLE III*.

Once the necessary materials were generated within the Crosslight software, the lead-based was constructed using the geometry in *FIGURE 5* and the parameters in *TABLE III*. However, the defect densities were omitted due to limited knowledge of the Crosslight software.

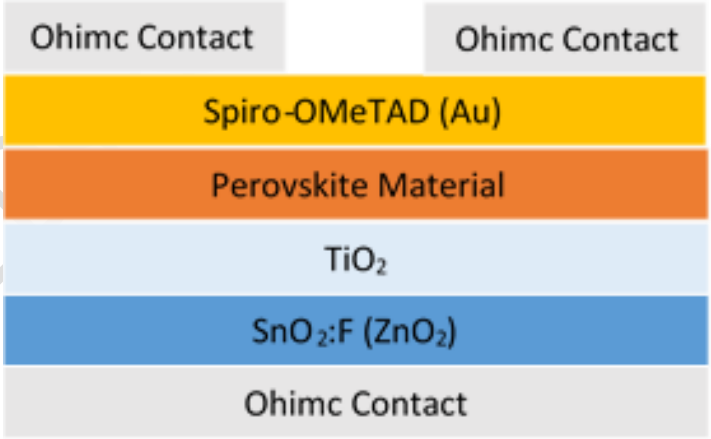


FIGURE 5: General structure of perovskite solar cell within Crosslight software. The width of each cell is 6 um. Thicknesses of each layer and perovskite material will vary based on the perovskite absorber being investigated. The materials in parentheses are the names used within the software.

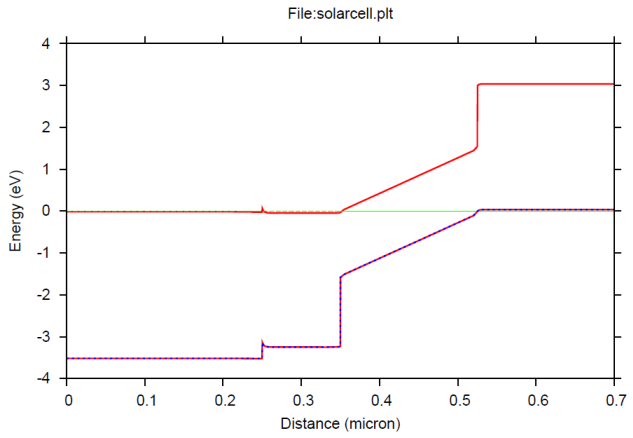
The first attempts at simulating using the parameters in *TABLE III* did not produce desirable results with short-circuit current, open-circuit voltage, and efficiency all being below the recorded values of the simulation by Minemoto and Murata. The solar cell parameters (thickness and doping) were adjusted in attempt to match the results. The final parameters are shown below in *TABLE IV*.

TABLE IV: Final simulation parameters of lead-based perovskite solar cell within the Crosslight software.

Parameters	**SnO_2:F (TCO)**	**TiO_2 (buffer)**	**IDL1 (defect layer)**	**$CH_3NH_3PbI_{3-x}Cl_x$ (absorber)**	**IDL2 (defect layer)**	**Spiro-OMeTAD (HTM)**
Thickness (nm)	250	100	5	165	5	175
N_A (cm^{-3})	-	-	-	-	-	$2x10^{19}$
N_D (cm^{-3})	$2x10^{19}$	10^{19}	10^{14}	10^{14}	10^{14}	-

After adjusting the thickness of each layer and the doping of each layer a maximum efficiency for the lead-based perovskite solar cell was achieved. All other parameters remained constant. These results are shown below in *FIGURE 6* and *TABLE V*. All simulations in Crosslight were first run solving for the equilibrium position and then using a light source providing 963.56 W/m^2 and sweeping the voltage to generate J-V curves.

a)



b)

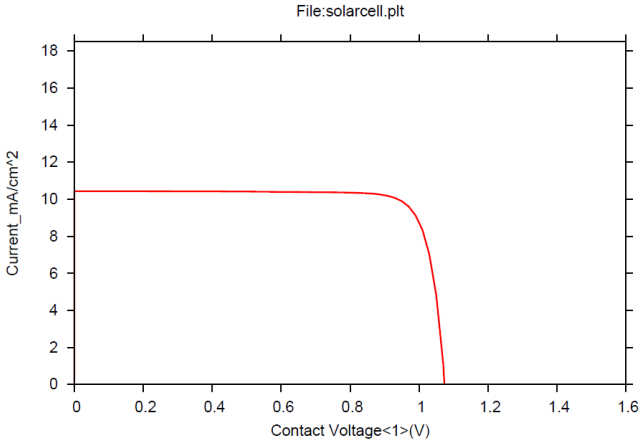


FIGURE 6: Simulation results of lead-based perovskite from Crosslight software a) Energy Band Diagram. b) J-V curve

TABLE V: Simulation results of lead-based perovskite from Crosslight software

Parameter	**Value**
Efficiency	9.75 %
I_{SC}	10.43 mA/cm^2
V_{OC}	1.07 V
V_M	.9482 V
I_M	9.909 mA/cm^2
FF	58.7 %

These results show that the energy band diagram is similar to the band diagram from Minemoto and Murata. However, this simulation was not able to meet the short-circuit current density, efficiency, and fill factor requirements originally proposed above. This could be a result of different test conditions that are not discussed within the paper by Minemoto and Murata. These test conditions could involve different

illumination, device geometry, or the differences of each simulation software. Despite these differences, the Crosslight simulation gave a baseline to compare the lead-based perovskite solar cell with its lead-free alternatives.

To compare the lead-free perovskite solar cell to the lead-base perovskite solar cell simulations will be performed using the same general structure as in *FIGURE 5*. This is done because multiple sources support very similar structures for various perovskite solar cells[11,13-18]. Due to the large number of possible combinations of lead-free perovskite solar cells, the materials will be limited to:

- A = Cs
- B = Sn, Ti, BiAg
- C = I, Br, Cl

These materials were chosen because of the available information found online. In addition, these will eliminate the factor of changing the organic cation in the absorption layer. It also allows for the ability to test Halide Double Perovskites by looking at materials containing BiAg. This gives 9 different lead-free perovskite solar cells to simulate. These simulations were done using as many absorber characteristics as possible found online. If parameters were not found, they were left the same as the lead-perovskite baseline test. This was done because it was extremely difficult to find this information online due to the perovskite solar cells just now gaining attention. Absorber characteristics are contained below in *TABLE VI*.

TABLE VI: Absorber characteristics for lead-free perovskite solar cells. Highlighted text are the characteristics that remained the same from the lead-based perovskite solar cell baseline simulation

Material	**E_g (eV)** [18,20,21]	**ε_r** [19]	**m^*_e** [19,20]	**m^*_h** [19,20]	**$\frac{\mu_n}{\mu_p}(\frac{cm^2}{Vs})$** [19]	**$X\ (eV)$ (Affinity)** [18]
$CsSnBr_3$	1.75	32.4	0.084	0.082	2.0/2.0	4.6
$CsSnI_3$	1.27	48.2	0.09	0.069	2.0/585	3.62
$CsSnCl_3$	1.52	29.4	0.09	0.14	2.0/2.0	3.9
$Cs_2BiAgCl_6$	2.7	6.5	0.34	0.31	2.0/2.0	3.9
$Cs_2BiAgBr_6$	2.3	6.5	0.28	0.21	2.0/2.0	3.9
Cs_2BiAgI_6	1.6	6.5	0.13	0.19	2.0/2.0	3.9
Cs_2TiBr_6	1.8	6.5	0.09	0.71	2.0/2.0	3.9
Cs_2TiI_6	1.65	6.5	0.09	0.71	2.0/2.0	3.9
Cs_2TiCl_6	3.4	6.5	0.09	0.71	2.0/2.0	3.9

After examination of this table, as the halide material increases in atomic number the band gap decreases. This is expected because at higher atomic numbers it requires less energy to pull an electron from the atom. The Halide Double Perovskites (Cs_2BiAgX_6) also have much higher bandgaps on average compared to the other perovskite materials.

Once all the absorber parameters were set, each lead-free perovskite solar cell was simulated to achieve its best efficiency by changing the thickness and doping of each layer. The final simulation parameters can be found in the ".layer" files within my simulation files folder. This folder will also contain energy band diagrams and J-V curves for each perovskite solar simulation in this report. The J-V curve characteristics are shown below in *TABLE VII*.

TABLE VII: Simulation results for lead-free perovskite solar cells.

Material	Efficiency	I_{SC} (mA/cm^2)	V_{OC} (V)	V_M (V)	I_M (mA/cm^2)	FF
$CsSnBr_3$	8.8 %	8.84	1.33	1.03	8.29	72.6 %
$CsSnI_3$	8.5 %	13.18	.995	.735	11.18	62.6 %
$CsSnCl_3$	14.12 %	13.34	1.23	1.09	12.46	82.77 %
$Cs_2BiAgCl_6$	4.65 %	2.899	2.2	1.61	2.78	95.9 %
$Cs_2BiAgBr_6$	9.76 %	5.98	1.84	1.64	5.74	85.6 %
Cs_2BiAgI_6	15.9 %	16.2	1.18	1.01	15.18	80.2 %
Cs_2TiBr_6	12.1 %	10.8	1.3	1.15	10.14	83.1 %
Cs_2TiI_6	12.5 %	12.8	1.2	1.01	11.98	78.8 %
Cs_2TiCl_6	.68 %	.45	1.9	1.57	.42	77%

This information shows that 5 of the lead-free perovskite solar cells have an efficiency equal or greater than the lead-based perovskite solar cell. With 4 of them being above the proposed 10% mark. Other outliers include Cs_2TiCl_6 which had a band gap too large to absorb any photons. $Cs_2BiAgCl_6$ also had a very high fill factor meaning it operates very close to its maximum power always.

Even though these results might show great potential for many lead-free perovskite solar cells, there are still many aspects missing from these simulations. Many of these devices in the real world only show efficiencies less than 5%. To improve the simulations, there must be a better understanding of the physics behind perovskite solar cells. This will allow the ability to have more precise simulations. Allowing simulated devices to behave very similar to the real devices. This could be achieved by simulating real world aspects such as defects or surface recombination. Perovskite solar cells have progressed so rapidly that this brute force method does not work without the information required to fully optimize these devices.

To improve these simulations more device parameters must be considered. In addition, these simulations do not account for the optical properties of these devices. It would also be important to simulate the inorganic cation oxidizing. This oxidation is a main contributor in why perovskite solar cells are unstable. Being able to simulate these factors will allow scientists to better understand what causes instability and to achieve a better understanding of these solar cells.

4. SUMMARY AND CONCLUSIONS

Perovskite solar cell technology has made large advances and will continue to make advances as researchers understand more about the physics behind these devices. These solar cells could potentially become a market competitor with multi- and single-crystalline silicon, CIGS, and CdTe solar cells because of their already competitive efficiencies and their potential to be produced at very low costs. If the problems of toxicity and stability are solved lead-free perovskites could easily begin to dominate the market. This would make solar energy even more competitive in the larger energy market by having prices close to their coal and fossil fuel counterparts.

Lead-free perovskite solar cells could potentially solve both of these issues by removing lead from these solar cells. These simulation results in Crosslight TCAD software show a slight potential that lead-free perovskites could compete with their lead-based counter parts. However, due to perovskite solar cells being in a very elementary stage, more information concerning these materials must be known to achieve a full picture on how these devices truly operate. This will allow the ability to see if lead-free perovskite solar cells are truly competitive with their lead-based counter parts.

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