Absorption study on the effect of mixed cation on tin and germanium-based perovskite solar cells

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Abstract. The thin film industry has been introduced with an invention of lead-based perovskite solar cells which eventually has gained a huge attention throughout the years. As the concern arises, this lead-based perovskite solar cells contributed towards both the environmental and human health issues due to the high level of toxicity. This then carve the paths into the research in finding suitable alternative for lead-free perovskite where tin and germanium are proposed as possible substitute, but the long-term durability and stability of both perovskites are still a challenge to be improved and maintained. In this study, tin and germanium-based solutions are fabricated individually with mixed cations of FA\(^{x}\)MA\(^{1-x}\)SnI\(_3\) and FA\(^{x}\)MA\(^{1-x}\)GeI\(_3\) in variations (1≤ x ≤0). The UV-Vis spectroscopy was analyzed in 400-1100 nm range to measure the light intensity absorption of full encapsulated fabricated perovskite solar cells after 30 days of exposure to surrounding conditions and recorded highest peak of absorption at the wavelength of 400 nm and 550 nm for tin based and germanium-based perovskite respectively.

1. Introduction

In 2050, global energy needs are predicted to increase as the world’s population grows. As a result, sustainable energy wind energy, hydro, and solar power becomes a pressing necessity. As a result, solar cells with longer stability term, high performance, using low cost materials and low environmental impact have become the subject of current energy research. [1] Perovskites are a group of organic compounds with a peculiar ABX\(_3\) structure that has made its way into solar cells as a light-absorbing film. The perovskite solar cells (PSCs) have gained popularity over the years due to its simplicity of fabrication, greater conductivity, and small band gaps. In particular, the formula term ABX\(_3\) refers to a type of crystalline material known as perovskites [2]. As these two sites are so dissimilar in size, the occupancy of these sites is mostly regulated by ionic size rather than valence, hence isostructural or isostructural cations can be used to selectively replace either the A or B ion. This allows a scientist to
change the characteristics of a particular oxide by incorporating certain cations to either the A or B surface [3].

Lead is found as a major component in most of the halide perovskite and has shown a great and effective performance as one of the photovoltaic materials, unfortunately is also a major area of concern upon the production of perovskite nowadays [4]. The high level of toxicity and the instability of lead element on the fabrications of perovskite, eventually hinder their commercialization and thus contribute towards the disadvantage in using lead halide perovskite materials as lead has a major impact on the resources of soil and water, also contributed towards greenhouse gas emissions [5].

The Goldschmidt tolerance factor, which is used to forecast the formability and stability of a perovskite structure, along with ionic size comparisons, identified a variety of potential cations as replacements in perovskites. These elements such as (e.g., Sn\(^{2+}\), Ge\(^{2+}\)), lanthanides (e.g., Eu\(^{2+}\), Yb\(^{2+}\)), transition divalent metals (such as Cu\(^{2+}\), Zn\(^{2+}\) etc.), alkaline earth metals (such as Mg\(^{2+}\), Ca\(^{2+}\) etc.) which are classified in Group 14 on periodic table of chemistry are found to be possible alternatives to produce lead free perovskite solar cells. Moreover, the absorber layer of perovskite that includes or consists of silicon, tin, germanium or either two of the cations found to be suitable replacement for lead free perovskite after reviewing the photovoltaic performance [6-7]. The rapid advancement of low-cost, high-efficiency hybrid perovskite solar cells has recently dominated the field of photovoltaic research. Considering significant advancements in the efficiency of such devices, achieving long-term material and device stability continues to be a challenge. Organic cations, where methyl ammonium-free devices were shown to have superior stability compared to their counterparts, and hole transport layer (HTL) materials, where poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) was shown to have a detrimental effect on thermal stability, are also factors to consider. [8]

2. Methodology
In this study, halide-based perovskite composition of manufactured devices containing dual cation (FA-MA) mixed with only tin and only germanium solutions are studied and done in a nitrogen glovebox. The primary part prioritized is the tin and germanium perovskite solution preparation. Firstly, FA and MA concentration are prepared individually to gained pure solutions of FA(B)I\(_3\) and MA(B)I\(_3\) at a volume ratio of x = 1 to where B is the material of tin and germanium. After developing pure concentration of FA(B)I\(_3\) and MA(B)I\(_3\) for only tin and only germanium the solutions are then mixed together according to their own class of material separately to achieve perovskite solutions which will form variations of FA\(_x\)MA\(_{1-x}\)SnI\(_3\) and FA\(_x\)MA\(_{1-x}\)GeI\(_3\). Next, the substrates are then prepared.

Coated FTO glass substrate or also known as fluorine-doped tin oxide substrate were cleaned by sonication method and dried by using nitrogen gas (N\(_2\)) purging technique and then coated with layer of TiO\(_2\) before being spin coated at 3000 rpm for 30 seconds with perovskite solution mixture followed by annealing process at temperature of 70 °C. Layer of PEDOT-PSS, the aqueous solution of hole conveying material, which has been filtered with a 0.45μm PVDF filter was also spin coated onto the substrate with the same speed and annealed at 140°C for 20 minutes. Thin platinum (Pt) material is then being spread on top of the previous layering that work as an electrode material. Small drop of epoxy is used to glue the last layer of perovskite which is the glass slips and being cured under UV light which is a process done to encapsulate the fabricated samples. Figure 1 shows the layering illustration for the perovskite solar cells. Samples are then being taken out from the nitrogen glovebox kept in a small container individually and are exposed to surroundings condition and room temperature.
Figure 1. Cross sectional layers of fabricated perovskite solar cells.

3. Results and Discussion

Presently, two techniques are being explored in order to enhance air-processed perovskite solar cells: (i) identify specific and simple manufacturing processes for producing high-quality perovskite films in ambient air; and (ii) develop new perovskite materials with naturally superior air stability [9]. The samples were taken out from the nitrogen glovebox, kept, and then tested after 30 days of exposure to surrounding conditions and room temperature. Figures 2 and 3 are the image of the fully fabricated and encapsulated perovskite solar cells for this research. The inconsistent spread of PEDOT: PSS onto the substrate can clearly be seen and this can be the cause affected the light intensity absorption of the perovskite solar cells as they are not equally spread onto the wide surface of FTO glass substrate.

PEDOT: PSS known as poly(3,4-ethylenedioxythiophene) have a condition of thick almost gel like consistency which more likely should be diluted to achieve a good concentration. Increased solubility of solutions resulting in significantly improved perovskite layer coverage on substrate. Also, due to the difficulties in controlling the formation rate constant for the perovskite layer, the one-step spin-coating approach usually results in poor film coverage.

Figure 2. Fully fabricated tin (Sn) perovskite solar cells.  
Figure 3. Fully fabricated germanium (Ge) perovskite solar cells.

The viscosity of precursor and the hydrophilicity or hydrophobicity of the surface to be coated are the most important factors in spin coating. Alas, utilising a simple spin coating to prepare the perovskite layer makes it challenging to achieve a uniform thickness across a wide area. The not uniform depositions will also produce defects in fabrications. Defects have a substantial impact on perovskite solar cell attributes, since they can affect critical parameters and processes such charge transport, charge recombination, power conversion efficiency, and stability. It's critical to know how stable the perovskite absorber is under technologically relevant environmental conditions. It's crucial to evaluate the
combination effects of light, oxygen, and moisture on the stability of perovskite films and devices in this environment also applies to material stability: disorganized and rough perovskite coatings increase the material's surface area, exposing it to oxygen and moisture [10].

The colour of fabricated substrates found to be quite light and sheer that may have affected the UV-vis results. According to earlier research, a tiny quantity of methylammonium (MA) cation is mixed with formamidinium (FA) to create $\text{FA}_x\text{MA}_{1-x}\text{GeI}_3$ perovskite, that favours the creation of the photoactive FA cation layer and results in high system efficiency [11]. Nevertheless, even with the insertion of MA cations, achieving plain black phased FA perovskite with no sign of yellow phased FA perovskite is still difficult due to the greater ionic radius of FA cations, especially albeit a considerable volume of FA is utilised as previously described [12]. Unfortunately, after attaining phase stability of FA dependent perovskite materials by combining halide ions, various research on photoinduced phase separation in mixed halide perovskite materials have been published and as advancement in Sn-based perovskite materials and solar cells has demonstrated that the PCE of $\text{FA}\text{SnI}_3$ solar cells are superior to that of $\text{MASnI}_3$, replacing MA with FA in A-site may be a useful technique. It has been linked to differences in the role of FA and MA in Sn halide perovskites' defect characteristics. [13-15]. The exceptional light-harvesting ability and high charge-carrier mobilities of hybrid perovskite materials like methylammonium lead iodide are responsible for perovskite-based electronics’ incredible performance [16].

Figure 4 and 5 shows the UV-Vis spectra graphs that are obtained from the tin and germanium perovskites respectively. It shows that most of the data gained are in negative values under visible lengths of 400-1100nm. However, it can also be seen that there are two obvious variations of perovskites that managed to sustain their absorption value above 0 after the 30 days period. The first perovskite is $\text{FASnI}_3$ in Figure 4 which achieved the highest absorption of 0.3018 a.u at 401nm and then maintained the absorption value in range no less than 0.0600 a.u. According to past research, optical absorption spectra of the $\text{FASnI}_3$ perovskite films with a higher FA ratio, the absorption wavelength drops, and the absorption edge gets sharper, indicating that the optical absorption coefficient rises [17]. For germanium perovskite in figure 5, $\text{FA}_{0.25}\text{MA}_{0.75}\text{GeI}_3$ variation is found to hold the highest absorption of 0.1955 a.u at 541 nm and were maintain above 0 with lowest range of 0.0138 a.u at 1100nm. Based on previous study, the absorption peak of the Ge-based perovskites with similar variations was seen in the visible light range of 520 to 620 nm. The Ge-based perovskites' photoluminescence profile revealed emission peaks in the range of 548 to 626 nm, with observed band gaps ranging from 2.26 to 1.98 eV [18].

Results obtained from this study shows, decrease in absorption value that also relates to the low efficiency production that will be obtained from the perovskites devices. The low absorption value indicates that the devices have loses it stability and capability over time. There are many factors that may have contributed towards these findings. Clean FTO glass substrate was used as a reference zero to conduct UV-Vis’s analysis and referring to past study, The FTO glass substrate's optimum transmittance was around 80%, according to the experimental results (for 500 nm thickness). The maximum transmittance was determined to be over 90% at a wavelength of roughly 500 nm [19]. As the absorption values of perovskites gained in this study are mostly negative it reflects that the light absorption for perovskites is less than the absorption of FTO glass itself.
Figure 4. Absorption spectra for tin (Sn) perovskites $\text{FA}_x\text{MA}_1-x\text{SnI}_3$.

Figure 5. Absorption spectra for Germanium (Ge) perovskites $\text{FA}_x\text{MA}_1-x\text{GeI}_3$. 
During the analysis, a clean FTO glass without any other deposit layers are set as reference value. The samples may have also experienced degradation process naturally once it was taken out from the nitrogen glovebox. Even though the perovskites solar cells have been encapsulated, the changes in surrounding temperature can increase the humidity levels allowing water to be permeated through the epoxy layer then eventually leads towards the degradation process. The presence of tiny air bubbles may also be the reason to the current errors. Therefore, full fabricated perovskite solar cells should be kept in an ambient condition, until it is ready to be used to preserve the durability.

4. Conclusions
The maximum absorption value at visible range gained by tin-based and germanium-based perovskites through UV-Vis spectra recorded at 400 nm and 540 nm respectively. Both type of perovskite can maintain stability over time at minimum range upon exposure to surrounding temperature, but low absorption value gained from both type of perovskites contributes to the prediction of low efficiency generations that might be produce in future. To study further about the stability of perovskites based on tin and germanium, the two main materials used in producing this lead-free perovskite solution are suggested to be mixed as mixed halide perovskites may increase the rate of efficiency and stabilize the device for long-term usage. It is also advisable to keep the fabricated perovskite under ambient conditions to lower the risks of degradation and elongate the lifetime of devices.

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