Particle Size Improvement and Layer Absorption of Methyl Halide MAPbI₃ Perovskite Doping Phenethylammonium Iodide (PEAI)

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ABSTRACT

This study aims to determine the effect of phenethylammonium iodide (PEAI) doping on grain size and absorption of the methylammonium lead iodide (MAPbI₃) perovskite layer. The MAPbI₃ perovskite layer is interesting to study because of its potential application in perovskite solar cells. In this study, the preparation of MAPbI₃ perovskite layer with PEAI doping variation using a 2-step spin-coating method. The surface morphology of MAPbI₃ shows an increase in grain size with the addition of PEAI doping variation. The optimum grain size is shown by adding 1.0 mg/ml PEAI doping variation, which is 117 ± 1.19 nm with a smooth surface morphology and tends to be homogeneous. X-ray diffraction (XRD) results on Perovskite MAPbI₃ showed no difference in peaks with the addition of PEAI doping. However, there is only a slight angle shift of 2θ, 0.05° at the main peak (110) and (220), so it will not change the cubic structure of MAPbI₃ crystal. The ultra violet visible (UV-Vis) graph shows an increase in absorbance of Perovskite MAPbI₃ with the addition of PEAI doping in the wavelength range of 400-550 nm. This research is expected to be a foundation for developing more efficient and stable solar cells.

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1. INTRODUCTION

Perovskite layers in recent years have become a very promising research subject due to their potential in various technologies, such as renewable energy and optoelectronics. Perovskite layers can produce solar panels with very high solar energy conversion efficiency in solar panel technology. Since they can absorb sunlight in a broad spectrum, they can produce more energy from the same light source (Green et al., 2014). Compared to conventional solar technologies such as silicon, the production of perovskite layers is cheaper and more accessible. This can reduce the cost of solar devices and accelerate the adoption of renewable energy (Kojima et al., 2009). In addition to being used in solar panels, perovskite layers can be used in various devices, such as light emission diodes (LED), light detectors, solar fuel cells, and other optoelectronic devices. Perovskite coatings can be used on surfaces, including transparent, flexible, or even printed surfaces (Yang et al., 2015).

Perovskite is a material with a chemical structure of ABX₃, where part A is organic cations such as CH₃NH₃ (MA) or monovalent inorganics such as Cs⁺ and Rb⁺. Part B is divalent metal cations such
as PbI$_2$, Ge$_2$, etc. Part X is a halide anion such as I$^-$ and Br$^-$ (Desoky et al., 2021), when applied to solar cell technology is still an important topic to be resolved. Modification and improvement of the physical properties of perovskite layers are the main factors needed to solve this efficiency problem. Doping the MAPbI$_3$ (methylammonium lead iodide) perovskite layer is an important strategy to change or improve the properties of the perovskite material. Doping can improve the performance of optoelectronic devices such as solar panels, light detectors, and light emission diodes (LED). This is because doping can affect the conductivity, photoluminescence efficiency, stability, and other optical properties of perovskites (Xiao et al., 2020). The electrical conductivity of perovskite can be enhanced with dop materials that have high charge mobility. This is important for applications such as solar cells and electronic devices (Hu et al., 2019). Doping the material can also improve the absorption ability of the coating to sunlight (Samanta et al., 2023).

Based on previous research (Zhang et al., 2017) doping FA elements into perovskite MAPbI$_3$ obtained a change in particle grain size to be larger than the control sample. However, the absorption results have yet to show a significant change. They are still in the same absorption range of 2.0-2.5 a.u., so when applied to solar cells, they still do not show high energy conversion, only increasing by about 10%. Previous research (Aharon et al., 2014) added MABr compounds to MAI to do Br doping on site I, but the results of the absorption ability decreased. So, it is necessary to look for alternative compounds to improve the physical quality of the MAPbI$_3$ perovskite layer.

Phenethylammonium iodide (PEAI) is an organic compound consisting of positive phenethylammonium ions (PEA+/$\text{C8H11NH3+}$) and negative iodide ions (I$^-$) that are very suitable for MAPbI$_3$ Perovskite layers. PEA+ shows very interesting performance in terms of physical engineering, as previously done. PEA+ is used as the main precursor in the preparation of PEA2FA4Sn5I16 perovskite layers and shows active properties interacting with other materials such as Ac- and BF4- resulting in physical properties that are very different from the initial properties where there is a change in shape in terms of particles as well as changes in particle grain size (Li et al., 2022). In addition, the energy conversion is amazing when PEA+ is engineered with Ac- and BF4-, where the efficiency increases from 1.41% to 8.11%. Therefore, this unique property of PEA+ will be something different when PEAI becomes a doping material in a more stable and high-performance perovskite system, namely MAPbI$_3$ (Roy et al., 2020). So, if PEAI is added to the MAPbI$_3$ perovskite structure, there will be a mix at sites A and X in the ABX$_3$ perovskite formula. This study will be different from previous studies where the ability to interact with PEA+, which is not a precursor but a doping material, will provide another factor in perovskite particle growth and absorption ability. PEA+ cations will fill the MA+ site in the MAPbI$_3$ structure, and strengthening will occur at the anion site. Therefore, in this study, the synthesis of MAPbI$_3$/CH$_3$NH$_3$PbI$_3$ (Methyl Ammonium Lead Iodide) perovskite layer added phenethylammonium iodide (PEAI) with PEAI concentration variations of 0 mg/ml (control device), 0.5 mg/ml, 1.0 mg/ml and 1.5 mg/ml using a two-step spin coating method that has shown amazing results (Ali Umar et al., 2023). Adding the PEAI solution to the MAI solution will improve the physical properties of the MAPbI$_3$ perovskite layer, thus opening up new ideas for developing perovskite solar cell technology.

2. METHOD

2.1 Preparation of Perovskite Precursors

Lead iodide and methylammonium iodide solutions were the precursors used in the MAPbI$_3$ perovskite coating. The lead iodide solution was prepared by dissolving 900 g of lead iodide powder (Aldrich) in a solvent mixture of 1.2 mL dimethylformamide (DMF) and 0.3 mL dimethyl sulfoxide (DMSO) (Ali Umar et al., 2023; Alias et al., 2021) on a hotplate at 60℃ and stirred using a magnetic bar at 700 rpm for approximately 4 hours. In addition, methylammonium iodide (MAI) precursor was prepared by dissolving 180 g MAI in 1 mL isopropyl alcohol (IPA) stirred at 700 rpm for 4 hours at room temperature. Phenethylammonium iodide (PEAI) stock solution was prepared at a concentration of 3 mg/mL in IPA and dissolved with an ultrasonic cleaner for 30 min. Then, PEAI was added to the
prepared MAI solution to achieve concentrations of 0.5, 1.0, and 1.5 mg/ml the Equation using Microsoft Word's Equation Editor (Microsoft Equation 3.0 or later).

Figure 1. Morphology of MAPbI₃ perovskite layer for PEAI concentration 0 mg/ml (A), 0.5 mg/ml (B), 1.0 mg/ml (C) and 1.5 mg/ml (D) with 30,000 X magnification
2.2 Preparation of Perovskite Precursors

MAPbI₃ perovskite layers were grown by a two-step spin coating method on an ITO glass substrate. First, 80 mL of 0.1 M PbI₂ solution was dripped onto the substrate and spun for 60 seconds at 2200 rpm. After that, it was heated on a hot plate for 60 seconds at 100°C. After the PbI₂ layer was cooled to room temperature, about 0.5 mL of IPA was immediately dripped and then spin-coated under the same conditions as the PbI₂ layer preparation. This aims to reduce the solvent content (DMF and DMSO) in the PbI₂ layer. Next, 0.8 mL of 0.1 M MAI solution was mixed with PEAI solution (0.5 mg/ml to 1.5 mg/ml), and hexamine was dripped onto the PbI₂ layer media at 2200 rpm and then allowed to stand for 30 seconds. The perovskite layer is formed when the yellow PbI₂ layer turns black. Next, the layer was heated on a hot plate for 15 minutes at 150°C. This synthesis process was carried out in a glove box with a 20%-35% humidity.

2.3 Characterizations

The morphology and surface shape of the samples were examined with a Zeiss Supra 55VP field emission scanning electron microscope (FE-SEM) (Zeiss, Oberkochen, Germany) at 3.0 kV. In addition, the crystallinity of the cubic perovskite phase was identified by Bruker D8 advance X-ray diffraction (XRD) (Bruker AXS GmbH, Karlsruhe, Germany), CuKα irradiation (λ 1/4 1.541 Å). To measure the optical absorbance of pure and PEAI-doped MAPbI₃ perovskite, a Hitachi U-3900H UV-vis spectrophotometer manufactured in Tokyo, Japan, was used at room temperature in the wavelength range of 300 nm-900 nm.

3. RESULTS AND DISCUSSION

3.1 Morphological Characteristics

FE-SEM images of MAPbI₃ perovskite with PEAI addition show significant changes in surface morphology compared to pure MAPbI₃ perovskite. Pure MAPbI₃ perovskite generally shows a relatively smooth and small grain surface. In contrast, adding PEAI 0.5 mg/mL to 1.5 mg/mL shows that the grain surface becomes more compact and straightforward, and the particle size becomes more extensive. This is assumed by the interaction between PEAI and the surface of MAPbI₃ granules, which can change the growth of granules and surface structure. As seen in Figure 1 (A-C), from a PEAI concentration of 0 mg/ml to a PEAI concentration of 1.0 mg/ml, the morphology is similar to the surface of perovskite (Cao et al., 2021). This is expected because adding PEAI to the MAPbI₃ structure will remain the exact structure of the perovskite itself. These results also confirm the addition of PEAI as a doping material is better for maintaining particle growth orientation than in previous studies (Li et al., 2022), which resulted in a change in the direction of perovskite particle growth so that there will be a possibility of changes in the crystal structure of the perovskite. However, at a high concentration of 1.5 mg/mL, the cohesiveness of the grains began to decrease. The coating became rougher and contained a crack like structure on the surface of the coating. This shows that adding higher PEAI can damage the structure of perovskite. This result is similar to what was done by previous research (Zhang et al., 2017), where they reported that there was a change in the shape of the particle grains when the doping given was too high (above 20% FA doping), besides that the particles also became coarser. They looked like many cracks, and the layers resulting from growth were also not uniform. This can reduce the performance of the coating if applied to solar cells because the noncompact structure can result in current leakage. It means there is a maximum limit to the doping concentration for more uniform surface results. This study's PEAI doping of 1.0 mg/mL gave top results.

FE-SEM analysis was also used to measure the particle size. The results show that with the addition of PEAI, the particle size of perovskite MAPbI₃ tends to be more significant. This can be explained by the influence of PEAI on the kinetics of grain growth during the synthesis process. The particle size of pure MAPbI₃ is 95 ± 1.29 nm. Adding PEAI 0.5, 1.0, and 1.5 to the MAPbI₃ perovskite changes particle size which is 101 ± 1.21 nm, 117 ± 1.19 nm, and 133 ± 1.23 nm (shown in Table 1). This result is similar to what was done by previous research (Zhang et al., 2017), where they reported an increase in the grain size of the perovskite layer when doping material was added (in this case, the
doping used was the element FA) from the size of 160 nm for pure MAPbI₃ to 300 nm for perovskite doping 30% FA. Similar things were also reported by other studies (Almutawah et al., 2018), where there was an increase in the grain size of MAPbI₃ perovskite particles when Cd²⁺ doping material was added from 200 nm to 600 nm. This comparison further proves that the addition of doping can increase the grain size of MAPbI₃ perovskite. This comparison further proves that the addition of doping can increase the grain size of MAPbI₃ perovskite. However, the addition of PEAI looks more regular increase in particle size, so it is possible to more easily engineer the desired particle size compared to the addition of other materials, such as previous studies that tend to change the scope is difficult to control because of the very drastic growth in size changes. In addition, in the particle size distribution without and with the addition of PEAI, it can be observed that the particle size distribution becomes more homogeneous than what was done previously (Li et al., 2022), where particle growth in previous studies tended to be irregular. This indicates that the addition of PEAI can help reduce the variation of particle size in MAPbI₃ perovskite. A more homogeneous particle size distribution can improve the consistency and stability of the material in solar cell applications (Zhang et al., 2020).

<table>
<thead>
<tr>
<th>Perovskite Sample</th>
<th>Particles Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃ with PEAI 0.0 mg/ml</td>
<td>95 ± 1.29</td>
</tr>
<tr>
<td>MAPbI₃ with PEAI 0.5 mg/ml</td>
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</tr>
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<td>MAPbI₃ with PEAI 1.0 mg/ml</td>
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<tr>
<td>MAPbI₃ with PEAI 1.5 mg/ml</td>
<td>133 ± 1.23</td>
</tr>
</tbody>
</table>

### 3.2 Phase Characteristics

MAI solution will improve the physical properties of the MAPbI₃ perovskite layer, thus opening up new ideas for developing perovskite solar cell technology. Based on Figure 2, the XRD peaks were identified as planes (110), (200), (202), (220), (310), and (312) in both samples. XRD analysis showed maximum peaks at two prominent peaks at angles of 14.1° and 28.5°, located at the (110) and (220) planes, respectively, for the pure MAPbI₃ data. The XRD peak analysis shows that the phases formed in the coating are cubic, according to previous research (Zhang et al., 2017). In addition, in Figure 2, there are no other peaks, including the peak of the ITO layer, confirming that the perovskite layer grown is thick enough that the light cannot reflect for the ITO peak itself. In addition, both graphs have the same pattern, meaning that adding PEAI material to perovskite MAPbI₃ does not produce new unwanted elements.

XRD peak shifts for MAPbI₃ and MAPbI₃ samples with PEAI 1.0 mg/ml in the (110) plane in Figure 2 part B, it can be seen that when PEAI material is added, the peak shifts as far as 0.05° to the left and when viewed as a whole peak, it turns out that all peaks consistently shift to the left by 0.05°. If we look again that this shift is very small, this explains that the addition of PEAI does not change the crystal structure of perovskite MAPbI₃ as the addition of other doping materials reported in further research (Dahlan et al., 2017; Hardi et al., 2020). It can be assumed that the PEAI material is well substituted into the MAPbI₃ structure. Similar results were reported by previous research (Yang et al., 2018) where Mg doping on MAPb₃ perovskite also did not produce new peaks, only a peak shift to the left as the doping concentration increased. These results further strengthen the doping material, which can be substituted into the perovskite structure without changing the original structure. These results also corroborate the FE-SEM analysis, which reports that it will produce the same and homogeneous particle shape with the right doping concentration. This is expected to increase the charge production capability of the solar cell device itself.

The field number, peak angle, Full Width Half Maximum (FWHM) value, and crystal size synthesized without and with the addition PEAI 1.0 mg/ml can be seen in Table 2. FWHM value and crystal size were obtained using diffraction EVA application and scherer equation. The table shows a slight change in the FWHM value, although not so significant. When PEAI 1.0 mg/mL is added, the FWHM value becomes slightly wider from 0.324 to 0.355 and 0.310 to 0.353 than without adding PEAI. So that this results in a change in crystal size, where the crystal size becomes smaller around 2-4 nm.
minimal size change is assumed not to change the crystal structure of MAPbI₃ but indicates that PEAI managed to enter the structure and bind the crystal to become denser. This result is corroborated by previous research (Khan et al., 2022), Bi doping into the MAPbI₃ perovskite layer only changes the crystal size from 44.5 nm to 47.5 nm without changing the original crystal structure.

Figure 2. XRD pattern of MAPbI₃ and PEAI-MAPbI₃ with a concentration of 1.0 mg/ml (A), XRD pattern at plane orientation (110) (B)

Table 2 Crystal structure of perovskite PEAI-MAPbI₃

<table>
<thead>
<tr>
<th>Perovskite Sample</th>
<th>Field Number</th>
<th>Peak Angle</th>
<th>FWHM</th>
<th>Crystal Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>110</td>
<td>14.10</td>
<td>0.324</td>
<td>27.46</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>220</td>
<td>28.50</td>
<td>0.310</td>
<td>29.34</td>
</tr>
<tr>
<td>MAPbI₃ + PEAI</td>
<td>110</td>
<td>14.05</td>
<td>0.355</td>
<td>25.02</td>
</tr>
<tr>
<td>3 mg/ml</td>
<td>220</td>
<td>28.45</td>
<td>0.353</td>
<td>25.17</td>
</tr>
</tbody>
</table>

3.3 Optical Characteristics

Confirm the optical properties of the MAPbI₃ perovskite layer formed. It can be done by measuring the absorption ability of the perovskite layer with UV-Vis spectroscopy, shown in Figure 3. The figure shows that the absorbance value increases when it approaches the wavelength of 700 nm and so on in a minor direction, the peak when the wavelength is 550 nm to 400 nm. The wavelength range
is the wavelength range of visible light. It is known that 40% of the range of sunlight entering the earth is the wavelength of visible light (Austin et al., 2021), which further strengthens the great potential of this perovskite technology itself in utilizing a significant source of sunlight.

Figure 3. Graph of absorbance spectrum against wavelength (A), magnification results of UV-Vis characterization at wavelength 650-850 nm (B)

The absorption ability of the perovskite layer increases with the addition of PEAI material into the perovskite layer, as seen in Figure 3. In figure Part A, it can be seen that the addition of PEAI increases the absorbance value of the perovskite layer in the region of 400 to 550 nm. The increase in absorption ability is fantastic, where the sample with perovskite without adding PEAI is only in the maximum absorption figure of 2.0-2.3. However, when PEAI is added with various concentrations, the absorption value is in the maximum figure of 4.0-5.0. This increase in uptake is much higher when compared to previous research (Aharon et al., 2014; Zhang et al., 2017), where the previous research uptake value was still at 2.0-2.3. It is also better than what was done in another study (Li et al., 2022), where PEAI produced a maximum absorption value of 3.5, and the absorption value did not increase when PEA⁺ was combined with other materials. At the same time, the addition of PEAI as doping resulted in an uptake value close to 5.0 a.u. This is highly expected as it is assumed that PEAI will be used as a doping agent. This is desirable because it is assumed that the increase in absorption value will
significantly affect the performance, especially the increase in charge production of Perovskite solar cells themselves (Basumatary & Agarwal, 2020).

Figure 3, part B, shows the results of the enlarged image on a larger scale. When PEAI 1.0 mg/mL is added, the absorption edge of the perovskite material does not change, as shown in the figure. Adding PEAI into the perovskite lattice of MAPbI3 increases the resonance of ultraviolet interaction with the perovskite electronic system but does not significantly change the optical band gap of perovskite. As a result, the absorption of ultraviolet light increases. This result is reinforced by previous similar studies (Li et al., 2020) that report the addition of doping does not significantly change the energy bandwidth but increases the absorption ability.

4. CONCLUSION

PEAI compounds are suitable for doping materials in MAPbI3 perovskite layers because they are proven to increase particle size as the doping concentration increases. In addition, the particles produced also have a smoother and clearer grain surface. Particle distribution also shows a more homogeneous distribution, although when a higher concentration of PEAI is added (1.5 mg/ml), the particle surface becomes rougher and looks like cracks. In addition, adding PEAI as a doping material increases the absorption ability of the MAPbI3 Perovskite layer, which is higher than previous studies. Perovskite MAPbI3 with PEAI doping 1.0 mg/ml shows an increase in optimum physical properties, so it becomes a new hope in developing perovskite-based solar cell technology.

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REFERENCE


