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Exploring Electronic and Optical Properties of CH$_3$NH$_3$GeI$_3$

Perovskite: Insights from the First Principles

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Graphic Abstract
Abstract

The three phases for MAGeI₃ in different temperatures play an important role in hybrid organic-inorganic perovskites solar cells. Up to now, their intrinsic nature still lacks systematic study. In this work, we established the crystal structures of MAGeI₃ (MA⁺=CH₃NH₃⁺) with orthorhombic, tetragonal and cubic phases. The electronic and optical properties of MAGeI₃ with three crystal structures including band gaps, density of states (DOS), absorption spectrum and dielectric function are calculated using the density functional theory (DFT). The calculated results reveal that MAGeI₃ pervoskites show substantial stability, a similar band gap, high carrier mobility and outstanding optical properties compared with MAPbI₃. The electronic properties are computed by GGA+U, demonstrating that the band gaps of MAGeI₃ for orthorhombic, tetragonal and cubic phases are 1.60 eV, 1.58 eV and 1.54 eV, respectively. The calculated results are generally in accord with available reported experimental data. Since the band gaps of MAGeI₃ are appropriate, the absorption region covers almost the entire visible zone. Our work not only uncover screening new materials for solar cells, but also further understand the inherent properties of MAGeI₃.

Keywords: MAGeI₃; three phases; electronic properties; optical properties; GGA+U

1 Introduction

In the lastest few years, hybrid organic-inorganic halide perovskites based solar cells (PSCs) have gained much attention in optimizing the materials for its outstanding optical properties[1-4]. The power conversion efficiency (PCE) of perovskites based solar cells has already exceeded 20%
in just five years\textsuperscript{[12-49]}. Besides, PSCs have many excellent properties, including optimum band
gap with large absorption coefficients\textsuperscript{[10]}, direct band gap\textsuperscript{[11]}, low electron and hole effective
masses\textsuperscript{[12]} and long carrier lifetime\textsuperscript{[13]}. However, lead is such a toxic element that these materials
are not environmental friendly.

In order to find an element to replace Pb, scientists try their best to explore the potential
alternatives. Numerous studies found that replacement of Pb with Sn can obtain similar properties
with an energy gap of about 1.3 eV in both experimental and theoretical results\textsuperscript{[14]}, but the stability
of Sn\textsuperscript{2+} is still a problem\textsuperscript{[15]}. The instability of MA\textsubscript{2}Sn\textsubscript{3}I\textsubscript{6} is related to the oxidation of Sn\textsuperscript{2+} to Sn\textsuperscript{4+} in
the air, which may cause the changes of structures and then reduce the optical properties\textsuperscript{[16]}. Compared with Sn, Ge possess high stability and superior performances\textsuperscript{[17]}. Obviously, it is that
Ge is a potential replacement for Pb to improve the photovoltaic performances. Ge-based
perovskites show similar solid-state properties to the Pb and Sn-based perovskites\textsuperscript{[18, 19]}

Amount of computational works about Pb and Sn-based perovskites have been reported.
However, as a new potential substitute, Ge-based perovskite is still not been researched in detail in
theory, for which there are many difficulties in experimental study. Therefore, we systematically
study the band gap and the photovoltaic performances of MAGeI\textsubscript{3} in three phases including
orthorhombic, tetragonal and cubic phase, so as to provide more theoretical basis for the
experiment.

2 Computational details

All first principle calculations were conducted using DFT as implemented in the Vienna ab
initio simulation package (VASP) code\textsuperscript{[20]}. The electron exchanges and interactions were described
using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximations (GGA) functional\cite{21}. In the calculation, we employed a plane wave basis and set energy cut-off of 700 eV combined with the ultrasoft pseudopotentials. The electronic configurations are 3d4s4p for Ge, 5s5p for I, 2s2p for C, 2s2p for N and 1s for H. For the system’s primitive cells we used a $6 \times 6 \times 6$ k-point grid generated according to the Monkhorst-Pack scheme to sample the Brillouin zone in the calculations of the structural optimization and electronic properties. During the optimization of the geometries, all structures were allowed to relax. The total energy was iterated until energy on the atoms is less than $1.0 \times 10^{-5}$ eV. It is well-known that PBE gives an underestimated band gap. In order to have a better description for the fundamental band gap from DFT, we employed a GGA+U approach\cite{22} by setting the Coulomb parameter, $U$, to 4 eV and the exchange parameter, $J$, to 0 eV. The value of $U$ is bigger and the deformation of the material’s structure will be more serious, so the biggest value of $U$ is 4 eV in the calculations. The results show that the band gap of MAGeI$_3$ are in good accord with the experimental band gap when the value of $U$ is 4 eV. This method we employed can correct the underestimation of the band gap (typical for PBE), and its computational efficiency in comparison with the hybrid functional of Heyd–Scuseria–Ernzerhof (HSE06).

3 Results and discussion

3.1 Structures

The orthorhombic (Pna2) perovskites structure of MAPbI$_3$ is the low temperature ground state and hold the stability to 165 K\cite{23,24}. MAPbI$_3$ undergoes a first-order phase transition from the orthorhombic to the tetragonal (I4/mcm) phase at 165 K, which goes through a second-order
phase transition to the cubic (Pm3m) phase by 327 K\textsuperscript{[23,25]}. We computed three phases of MAGeI\textsubscript{3} in this study. To get appropriate structures of MAGeI\textsubscript{3}, we considered a typical useful parameter, the tolerance factor \( t \), to deduce the probable structures. We calculated \( t \) using the formula\textsuperscript{[26]}

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]

For an ABX\textsubscript{3} pervoskites, \( r_A \), \( r_B \) and \( r_X \) are the ionic radius of the corresponding ions. Here, we employed the effective radius of MA\textsuperscript{+} and I\textsuperscript{-} that previously reported\textsuperscript{[26,27]}, obtaining the value of \( t \) is 0.97. In general, \( t \) is in the range of 0.97~1.03 can reach an empirically ideal pervoskites structure. Obviously, the structures of MAGeI\textsubscript{3} are very close to an ideal pervoskites structure\textsuperscript{[28]}. The optimized stable geometries and lattice constants are shown in Figure 1 and Table 1.To confirm the obtained lattice parameters are surely valid, we evaluated potential surface for a, b, and c axes. For each direction, the potential energy curve is evaluated with the fixed other lattice parameters. The results are depicted in Figure S1 (see Supporting information). The potential energy of the optimized lattice parameters is the lowest. It can be concluded that the data is credible. We also optimized the structures of MAPbI\textsubscript{3} in the three phases. The result is in good accord with the experimental data with a range of 1\% - 2\%\textsuperscript{[29]}.
Figure 1 Crystal structures of (a) orthorhombic, (b) tetragonal, (c) cubic phases of MAGeI₃.

Table 1 Calculated lattice parameters for the MAMI₃ (M = Ge, Pb) perovskites.

<table>
<thead>
<tr>
<th>Sort</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>α/°</th>
<th>β/°</th>
<th>γ/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAGeI₃-c</td>
<td>6.12</td>
<td>6.11</td>
<td>6.15</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>MAGeI₃-o</td>
<td>8.77</td>
<td>8.61</td>
<td>11.41</td>
<td>90</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>MAGeI₃-t</td>
<td>8.44</td>
<td>8.44</td>
<td>12.53</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>
3.2 Electronic properties

The calculated band gaps for MAGeI\textsubscript{3} in three crystal structures listed in Table 2. The band gap is an important factor that determines many of physical properties. Taking account of both accuracy and time-consumption, we adopted the GGA+U method to calculate band gaps. A small band gap can cause a very broad absorption range. The calculated band gaps for the orthorhombic, tetragonal and cubic phase are 1.60 eV, 1.58 eV and 1.54 eV, respectively. Due to the small band gaps for MAGeI\textsubscript{3}, this material possess superior optical properties. And the band gap of MAGeI\textsubscript{3} matches well with that of MAPbI\textsubscript{3}.

<table>
<thead>
<tr>
<th>Material</th>
<th>orthorhombic</th>
<th>tetragonal</th>
<th>cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI\textsubscript{3}-c</td>
<td>6.33</td>
<td>6.33</td>
<td>6.33</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}-c (exp.) \textsuperscript{a}</td>
<td>6.28</td>
<td>6.28</td>
<td>6.28</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}-o</td>
<td>8.88</td>
<td>8.58</td>
<td>12.92</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}-o (exp.) \textsuperscript{a}</td>
<td>8.83</td>
<td>8.55</td>
<td>12.58</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}-t</td>
<td>8.93</td>
<td>8.93</td>
<td>12.97</td>
</tr>
<tr>
<td>MAPbI\textsubscript{3}-t (exp.) \textsuperscript{a}</td>
<td>8.80</td>
<td>8.80</td>
<td>12.69</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From Ref.[29]

Table 2 Calculated band gaps of MAXI\textsubscript{3} (M=Pb,Ge) pervoskites with the GGA+U method.
The conduction band minimum (CBM) and the valence band maximum (VBM) are all at the $\Gamma$ point in the three structures, manifesting that MAGeI$_3$ is a direct band gap semiconductor. As Figure 2 shown, the band structures of MAGeI$_3$ in the three phases are generally similar, and the band gaps of the three structures are in the range of band gap for excellent solar cells. The results indicated that MAGeI$_3$ perovskite is an outstanding material for solar cells.

<table>
<thead>
<tr>
<th></th>
<th>Band Gap (eV)</th>
<th>Band Gap (eV)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAGeI$_3$</td>
<td>1.60</td>
<td>1.58</td>
<td>1.54</td>
</tr>
<tr>
<td>MAPbI$_3$</td>
<td>1.74</td>
<td>1.62</td>
<td>1.73</td>
</tr>
</tbody>
</table>
To further probe the intrinsic nature of the electronic structures, the density of states for MAGeI\textsubscript{3} in three phases illustrated in Figure 3. The curves of DOS for each kind of structures are very similar. The Fermi energy is set as zero. In the range of -11 eV ~ -13 eV, there is a DOS peak, which consists of the I-5s and Ge-3s states. And then, a sharp DOS peak is located at the center of -8 eV ~ -6 eV, which predominately consists of the Ge-3p states. The main contribution of VBM to

Figure 2 Band structures of (a) orthorhombic, (b) tetragonal, (c) cubic phases of MAGeI\textsubscript{3}.  

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{band Structures.png}
\caption{Band structures of (a) orthorhombic, (b) tetragonal, (c) cubic phases of MAGeI\textsubscript{3}.}
\end{figure}
the three MAGeI$_3$ structures comes from the p orbitals of I, with the overlap of the s and p orbitals of Ge, while the CBM is dominated by the p orbital of Ge atoms.
Figure 3 DOS structures of (a) orthorhombic, (b) tetragonal, (c) cubic phases of MAGeI3.
And after in-depth study found the electrons distribute around the CBM as well as the holes are around the VBM. Due to the electrons and holes in the MAGeI$_3$ are thermally relaxed to the CBM and VBM, respectively, a small effective mass of the electrons and holes can facilitate the transportation. The effective masses of MAGeI$_3$ and MAPbI$_3$ are displayed in Table 3. By the following formula, we calculated the effective masses of $m_e^*$ and $m_h^*$.

$$m^* = \hbar^2 \left[ \frac{\partial^2 E(k)}{\partial k^2} \right]^{-1}$$

As shown in the equation, $k$ is the wave vector and $E(k)$ is the band edge eigenvalues. The effective masses of the electrons and holes for MAGeI$_3$ are generally smaller than them for MAPbI$_3$. The results indicate that MAGeI$_3$ pervoskite has higher carriers mobility.

<table>
<thead>
<tr>
<th>Sort</th>
<th>MAPbI$_3$-o</th>
<th>MAPbI$_3$-t</th>
<th>MAPbI$_3$-c</th>
<th>MAGeI$_3$-o</th>
<th>MAGeI$_3$-t</th>
<th>MAGeI$_3$-c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e^*/m_0$</td>
<td>0.198</td>
<td>0.264</td>
<td>0.097</td>
<td>0.156</td>
<td>0.244</td>
<td>0.109</td>
</tr>
<tr>
<td>$m_h^*/m_0$</td>
<td>0.124</td>
<td>0.168</td>
<td>0.145</td>
<td>0.071</td>
<td>0.163</td>
<td>0.127</td>
</tr>
</tbody>
</table>

### 3.3 Optical properties

For optical calculations, the optical properties can be determined by the dielectric function

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega),$$

where the real part $\varepsilon_1(\omega)$ can be obtained from the imaginary part $\varepsilon_2(\omega)$ using the Kramer–Kronig relation and the imaginary part $\varepsilon_2(\omega)$ can be evaluated from the momentum
matrix elements between the unoccupied and occupied wave functions. Other optical properties including the refractivity index \( n(\omega) \) and the absorption coefficient \( \alpha(\omega) = \varepsilon_2(\omega)/cn(\omega) \), \( c \) is the speed of light in \textit{vacuo} can be calculated by \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \). To further probe the optical properties of MAGeI\(_3\) pervoskites in the three phases, we calculated the absorbance and dielectric function for the three phases of MAGeI\(_3\). As show in Figure 4(a), the three phases of MAGeI\(_3\) show an appropriate absorbance in the visible zone (380 nm-780 nm). MAGeI\(_3\) pervoskites have a weak absorption in the ultraviolet spectrum and have a large red shift. Both the imaginary and real parts of dielectric function for the three phases are illustrated in Figure 4(b). The imaginary parts of the dielectric function for the computed structures display two peaks below 600 nm and then show a downward trend. The results in good agreement with the absorption spectrum. The absorption covers almost the entire visible light spectrum. Therefore, MAGeI\(_3\) pervoskite shows a good solar energy absorption in the visible light region.
Figure 4 Calculated (a) absorption spectra and (b) dielectric spectra of the MAGeI$_3$ systems. In the dielectric spectra, the imaginary parts are shown in dashed lines, and the real parts are shown in solid lines.

4 Conclusions

In this work, DFT method were used to study the electronic and optical properties for three crystal structures of MAGeI$_3$. In particular, we used the GGA+U method to correct the band gap. Firstly, the basic optimization procedure has been conducted. And then the electronic properties including band gaps, band structures and density of states have been obtained, which are accordance with available experimental data. Furthermore, the effective masses of carriers for MAGeI$_3$ are small, which leads to higher carriers mobility. Finally, the calculated optical properties of MAGeI$_3$ in orthorhombic, tetragonal and cubic structures manifest that MAGeI$_3$ pervoskites have good solar energy absorption in visible zone and have a red shift. The results
show that the photovoltaic properties of MAGeI\(_3\) are in generally agreement with MAPbI\(_3\)’s, therefore, Ge can be a promising substitute of Pb in MAPbI\(_3\) pervoskites based solar cells.

ACKNOWLEDGMENTS

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References


[29] T. Baikie, Y. Fang, J.M. Kadro, M. Schreyer, F. Wei, S.G. Mhaisalkar, M. Graetzel, T.J. White,
Highlights

► First systematically study the band gap of MAGeI$_3$ in three phases including orthorhombic, tetragonal and cubic phase.

► The band gaps of MAGeI$_3$ are appropriate compared to the MAPbI$_3$.

► the absorption of MAGeI$_3$ covers almost the entire visible scope.
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