A Dissertation

entitled

Optoelectronic and Defect Properties in Earth Abundant Photovoltaic Materials: First-principle Calculations

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in Physics

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An Abstract of
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In this dissertation, a series of earth-abundant photovoltaic materials including lead halide perovskites, copper based compounds, and silicon are investigated via density functional theory (DFT).

Firstly, we study the unique optoelectronic properties of perovskite CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$. First-principle calculations show that CH$_3$NH$_3$PbI$_3$ perovskite solar cells exhibit remarkable optoelectronic properties that account for the high open circuit voltage ($V_{oc}$) and long electron-hole diffusion lengths. Our results reveal that for intrinsic doping, dominant point defects produce only shallow levels. Therefore lead halide perovskites are expected to exhibit intrinsic low non-radiative recombination rates. The conductivity of perovskites can be tuned from $p$-type to $n$-type by controlling the growth conditions. For extrinsic defects, the $p$-type perovskites can be achieved by doping group-IA, -IB, or -VIA elements, such as Na, K, Rb, Cu, and O at I-rich growth conditions. We further show that despite a large band gap of 2.2 eV, the dominant defects in CH$_3$NH$_3$PbBr$_3$ also create only shallow levels. The photovoltaic properties of CH$_3$NH$_3$PbBr$_3$–based perovskite absorbers can be tuned via defect engineering. Highly
conductive $p$-type CH$_3$NH$_3$PbBr$_3$ can be synthesized under Br-rich growth conditions. Such CH$_3$NH$_3$PbBr$_3$ may be potential low-cost hole transporting materials for lead halide perovskite solar cells. All these unique defect properties of perovskites are largely due to the strong Pb lone-pair $s$ orbital and I $p$ (Br $p$) orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbX$_3$ (X=I, Br).

Secondly, we study the optoelectronic properties of Cu-V-VI earth abundant compounds. These low cost thin films may have the good electronic and optical properties. We have studied the structural, electronic and optical properties of Cu$_3$-V-VI$_4$ compounds. After testing four different crystal structures, enargite, wurtzite-PMCA, famatinite and zinc-blend-PMCA, we find that Cu$_3$PS$_4$ and Cu$_3$PSe$_4$ prefer energetically the enargite structure, whereas, other compounds favor the famatinite structure. Among the compounds and structures considered, enargite Cu$_3$PSe$_4$, and famatinite Cu$_3$AsS$_4$, are suitable for single junction solar cell applications due to bandgaps of 1.32 eV and 1.15 eV, respectively. Furthermore, CuSbS$_2$ are also studied by density functional theory and HSE06 hybrid functional. The chalcostibite CuSbS$_2$ has an indirect band gap of 1.85 eV, whereas the chalcogenide Cu$_3$SbS$_4$ has a direct band gap of 0.89 eV. We find that the large difference on band gaps is mainly attributed to the different Sb charge states. We further predict that the Sb charge states will affect the defect physics. Particularly, the Sb lone pair $s$ orbitals in CuSbS$_2$ have strong influence on the formation energies of Sb-related defects.

Lastly, we have studied the atomic structure and electronic properties of aluminum (Al)-related defect complexes in silicon. We find a unique stable complex configuration consisting of an Al$_i$ and an oxygen dimer, Al$_i$-2O$_i$, which introduces deep
levels in the band gap of Si. The formation energies of the Al\textsubscript{i}-2O\textsubscript{i} complexes could be lower than that of individual Al\textsubscript{i} atoms under oxygen-rich conditions. The formation of Al\textsubscript{i}-2O\textsubscript{i} complexes may explain the experimental observation that the coexistence of Al and O results in reduced carrier lifetime in Si wafers.
To my fiancé Bao,

Time flies, but you are always there for me

时光飞逝，却有你一直在守候
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List of Abbreviations

DFT............................Density functional theory
VASP .........................Vienna ab-initio simulation package
GGA..........................General gradient approximation
PAW .........................Projector augmented-wave
PV.............................Photovoltaic
CIS.........................CuInSe$_2$
CZTS.......................Cu$_2$ZnSnSe$_4$
S-Q.........................Shockley queissner
MA.........................Methyl ammonia
Chapter 1

General Introduction

Within four years, organic-inorganic MAPbI$_3$ solar cells have achieved the efficiencies as high as 20.1% now [1-2]. MAPbI$_3$ perovskite exhibits extremely high optical absorption coefficient and long electron-hole diffusion lengths[3-5]. It has clearly demonstrated its remarkable potential for producing high-efficiency and low-cost thin-film solar cells. Compared with the conventional inorganic thin film solar cell, perovskites have their unique optoelectronic properties, which are partially attributed to the strong Pb lone-pair $s$ orbital and I $p$ (Br $p$) orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbX$_3$ (X=I, Br) [5-8].

The perovskites show very unique defect properties, which are distinguished from other earth-abundant thin-film solar cell absorbers such as CuInSe$_2$ (CIS)[9] and Cu$_2$ZnSnS$_4$ (CZTS)[10]. In CH$_3$NH$_3$PbI$_3$, the dominant donor MA$_i$ and dominant acceptor V$_{\text{Pb}}$ have comparable formation energies[6]. Donors in CIS and CZTS generally have much higher formation energies than acceptors. The formation energies of donors Cu$_i$ and In$_{\text{Cu}}$ in CIS are more than 2 eV higher than that of acceptor V$_{\text{Cu}}$. Thus acceptor defect dominates the conductivity of CIS. In CH$_3$NH$_3$PbI$_3$ perovskite, the growth condition can be controlled to tune the dominate defects, from the dominant donor defect
MAi to the acceptor defect V\textsubscript{Pb}. The low formation energy of V\textsubscript{Pb} in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} is due to the energetically unfavorable s-p antibonding coupling, which resembles the p-d antibonding coupling in CIS [9]. The fully occupied antibonding state between Pb s and I p coupling does not gain electronic energy thus tend to bond break and form a vacancy. The lower formation energy of MAi could be explained by its weak van der Waals interaction with Pb-I framework.

Referred to as the earth abundant materials, copper based thin films always attract the research attention. Polycrystalline CuInSe\textsubscript{2}-, and Cu\textsubscript{2}ZnSnSe\textsubscript{4}-based thin-film solar cells have reached efficiencies of 21.7\%, and 12.7\%. Compared with the binary compounds, the ternary chalcogenide semiconductors exhibit more flexible properties due to their enhanced structural and chemical choice. Consider the doping and the defects properties, the ternary compounds do not have very complicated situation, which happened in quaternary compounds. Therefore, the electronic and structural properties of ternary I-III-VI\textsubscript{2} have been studied extensively. Beside I-III-VI\textsubscript{2}, there exist another ternary chalcogenide compounds that also obey the electron octet rule and consist of ACh\textsubscript{4} tetrahedron units: I\textsubscript{3}-V-VI\textsubscript{4}. The group-I elements are Cu and Ag, and the group-V elements include P, As, Sb, and Bi. The I\textsubscript{3}-V-VI\textsubscript{4} ternary compound semiconductors may also have the potential for electronic device applications. For example, Cu\textsubscript{3}PS\textsubscript{4} and Cu\textsubscript{3}PSe\textsubscript{4} have shown photoelectrochemical response.[11] Cu\textsubscript{3}V-VI\textsubscript{4} compounds has a wide band range when suitable for various solar cell applications.[12]

Although the development of current perovskite solar cells and copper based thin film technology is fast, the large scale commercialization of these earth abundant material based solar cells is still a challenge, compared with the traditional silicon manufactory.
Further investigations of optoelectronic and defect properties of these materials are necessary. If $p$-type MAPbI$_3$ and CH$_3$NH$_3$PbBr$_3$ can be realized in the experiment, the low-cost and high efficiency perovskites can be expected. CH$_3$NH$_3$PbBr$_3$–based absorbers show clearly the potential for achieving high efficiency and high $V_{OC}$ top cells. For the copper based thin films, their various band gap may be used to the multijunction solar cell technology, which is so far the only technology that has demonstrated efficiencies higher than the Shockley-Queisser limit for solar to electricity conversion efficiency. High efficiency tandem cells based on polycrystalline thin film semiconductors possess the most potential for producing low-cost solar electricity.
Chapter 2

Density Functional Theory and VASP

In our studies, first-principles calculation means ab initio methods (ab-initio calculation), refers to the calculation of integration of all electrons without any empirical parameters. It only uses three basic physics constants: plank constant, electron rest mass and electron charge, solving the electronic structure problem of multi-electrons system. Considering the inherent properties of materials, they finally depend on the atomic structures and their corresponding characteristics influenced by a periodic field of electrical, optical, magnetic potential.

Due to the discovery of electron diffraction in early 20th century, the scientists confirmed the 'wave-particle duality' nature of electrons from the experiments. In order to characterize this property, the corresponding quantum mechanics wave function \( \Psi (r) \) was introduced and found to satisfy the Schrödinger equation.

\[
\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi(r) = E\psi(r)
\]  

(2.1)

For single-electron systems, such as a hydrogen atom, the Schrödinger equation can be solved accurately, thereby solve the wave function, eigen-value and other physics parameters. However, for the multi-electrons system, how can we solve the Schrödinger equation and write the corresponding Hamiltonian. For the Schrödinger equation in
many-body systems in condensed matter, it also can be written as the equation of Hamiltonian

$$\hat{H}\psi(r_1, r_2, ..., r_N) = E\psi(r_1, r_2, ..., r_N) \tag{2.2}$$

where the specific form of the Hamiltonian can be further written as

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i\neq j} \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|} - \sum_{i\neq j} \frac{Z_i e^2}{|\vec{r} - \vec{R}_j|} \tag{2.3}$$

Here, the first term and the second term represents the electron kinetic energy and the electron-electron interaction; the third and fourth one stand for the kinetic energy of nucleus and the interaction among them; the last one is the interaction between electrons and nuclei.

Although we can write the Schrödinger equation of many-body system accurately, it is very difficult to solve this equation and get the corresponding physics parameters. In the real solid materials, there are $10^{29}$ electrons per cubic meter. The variables for solving the Schrödinger equation are enormous. Assumed we could use the single-electron wave function approximation, and incorporate the exchange-correlation effects into the Hamiltonian, we may solve the problems of many-body systems effectively.

### 2.1 Density Functional Theory

To solve the problems of multi-electrons system, density functional theory was mentioned by P. Hohenberg and W. Kohn in 1964 [13]. The key assumption of this theory is that the total energy of the ground state of the multi-electrons system can be written as one functional of the density charge in ground state. Based on this theory, Kohn and Sham will convert the original Schrödinger equation of multi-electron system
into a single particle Kohn-Sham equation through the variation method, which makes it possible to calculate the electronic structure of multi-electron system.

### 2.1.1 Hohenberg-Kohn Theorems

Hohenberg-Kohn theorem proving ground state energy and charge density of many-body problem have the one to one correspondence. This relation will simplify the many-body problem unthinkably. Hohenberg-Kohn theorems became the basis of the density functional theory, which are based on non-uniform electron gas theory and can be summed up into two aspects [13].

1. Theorem one - the external potential $\hat{V}_{ext}$, and hence the total energy, is a unique functional of the electron density $\rho(r)$. The energy functional referred can be written in terms of the external potential

$$E[\rho(r)] = \int V_{ext}(r)\rho(r)dr + F[\rho(r)]$$  \hfill (2.4)

where $F[\rho(r)]$ is an unknown functional. Based on the equation above, we can get the relation among the energy of system, wave function and the Hamiltonian

$$E[\rho(r)] = \langle \psi | \hat{H} | \psi \rangle$$  \hfill (2.5)

Where the Hamiltonian also can be written as

$$\begin{cases} \hat{H} = \hat{F} + \hat{V}_{ext} \\ \hat{F} = \hat{T} + \hat{V}_{ee} \end{cases}$$  \hfill (2.6)

In the formula above, $\hat{T}$ is the kinetic energy operator, $\hat{V}_{ee}$ is the operator of the interaction between electrons. If only summarized from the forms, we know operator $\hat{F}$
has the same effect to all electrons of this system, so the system Hamiltonian will be
mainly decided by the number of electrons $N$ and the external potential $\hat{V}_{\text{ext}}$.

Supposed there are two different external potentials $\hat{V}_{\text{ext}1}, \hat{V}_{\text{ext}2}$ which give the same
ground charge densities $\rho_1 = \rho_2 = \rho$. Under different external potentials, the
corresponding Hamiltonians $\hat{H}_1, \hat{H}_2$ and wave functions $\psi_1, \psi_2$ are different. According
to the variational principle, for the first wave function of ground state, we will have

$$E_1^0 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle < \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle = \langle \psi_2 | \hat{H}_2 - \hat{V}_{\text{ext}2} + \hat{V}_{\text{ext}1} | \psi_2 \rangle$$
$$= \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \hat{V}_{\text{ext}2} + \hat{V}_{\text{ext}1} | \psi_2 \rangle = E_2^0 + \int dr \rho(r) \left[ \hat{V}_{\text{ext}1} - \hat{V}_{\text{ext}2} \right]$$  \hspace{1cm} (2.7)

For the second wave function of ground state $\psi_2$, we will have

$$E_2^0 < E_1^0 + \int dr \rho(r) \left[ \hat{V}_{\text{ext}2} - \hat{V}_{\text{ext}1} \right]$$  \hspace{1cm} (2.8)

If we combined the equation (2.7) and (2.8) together, we get

$$E_2^0 + E_1^0 < E_1^0 + E_2^0$$  \hspace{1cm} (2.9)

Based on the previous assumption, we know the equation doesn’t make any sense.

Therefore, the assumption could not be established, and thus $\rho_1 \neq \rho_2$. Furthermore, it also
proves $\hat{V}_{\text{ext}}$ is the only functional of the charge density $\rho$. It means that if the charge
density of ground state is known, the external potential $\hat{V}_{\text{ext}}$, Hamiltonian $\hat{H}$ and the
corresponding properties of ground state will be uniquely determined.

(2) Theorem two - the ground state energy can be obtained variationally: the density that
minimizes the total energy is the exact ground state density.
The proof of this theorem is straightforward: as just shown, the ground state density $\rho(r)$ determines the external potential $\hat{V}_{\text{ext}}(r)$, the particle number $N$ and external potential $\hat{V}_{\text{ext}}(r)$ determine the Hamiltonian $\hat{H}$ and the wave function $\psi$, so the energy functional based on the known external potential is

$$
\begin{align*}
\left\{ \begin{array}{l}
E[\rho(r)] = \int dr \hat{V}_{\text{ext}} \rho(r) + F[\rho(r)] \\
F[\rho(r)] = \langle \psi | \hat{F} | \psi \rangle = \langle \psi | \hat{T} + \hat{V}_{\text{ext}} | \psi \rangle
\end{array} \right.
\end{align*}
$$

(2.10)

When the particle numbers is the same, the variational principle applies for the different wave function $\psi$ and $\psi'$

$$
\begin{align*}
\left\{ \begin{array}{l}
\langle \psi' | \hat{F} | \psi' \rangle > \langle \psi | \hat{F} | \psi \rangle \\
\langle \psi' | \hat{V}_{\text{ext}} | \psi' \rangle > \langle \psi | \hat{V}_{\text{ext}} | \psi \rangle
\end{array} \right.
\end{align*}
$$

(2.11)

This also leads to

$$
\langle \psi' | \hat{F} | \psi' \rangle + \langle \psi' | V_{\text{ext}} | \psi' \rangle > \langle \psi | \hat{F} | \psi \rangle + \langle \psi | V_{\text{ext}} | \psi \rangle
$$

(2.12)

So

$$
F[\rho'(r)] + \int V_{\text{ext}} \rho'(r) dr > F[\rho(r)] + \int V_{\text{ext}} \rho(r) dr
$$

(2.13)

Also from the equation (2.12), we can obtain

$$
E[\rho'(r)] > E[\rho(r)]
$$

(2.14)

where $\rho(r)$ is the charge density of ground state, formula (2.14) further indicated that if the charge density of ground state is determined, so it will give the minimum value of the energy functional, which is the enery of ground state $E[\rho]$.

Hohenberg-Kohn theorems prove the relation between the charge density and the ground state. This theorem is indeed a breakthrough for solving the many-body problems,
but it does not give the methods to solve the charge density of the ground state. Then in 1965, W. Kohn and L. J. Sham method[14] was proposed for solving the ground state charge density.

### 2.1.2 Kohn-Sham Method

According to Hohenberg-Kohn theorems, we can obtain the energy of ground state through variation of the functional density to the charge density, under the conservation condition of the particle number \( \int dr \delta \rho(r) = 0 \),

\[
\begin{align*}
\delta \left[ F[\rho(r)] + \int V_{\text{ext}}(r) \rho(r) dr - \mu \left( \int \rho(r) dr - N \right) \right] &= 0 \\
\mu &= \frac{\delta F[\rho(r)]}{\delta \rho(r)} + V_{\text{ext}}(r)
\end{align*}
\]

(2.15)

where \( \mu \) is the Lagrange multipliers, corresponding to the chemical potential, F functional contains three parts as below,

\[
\begin{align*}
F[\rho(r)] &= T[\rho(r)] + E_{C}[\rho(r)] + E_{\text{ xc}}[\rho(r)] \\
E_{C}[\rho(r)] &= \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{r-r'} drdr'
\end{align*}
\]

(2.16)

The first term of F functional represents the kinetic energy functional of non-interaction electrons, the second term is the Coulomb interaction, the last one is the exchange-correlation energy. For the last one, it cannot be obtained precisely, because all left complex and unsolvable factors are included into this exchange-correlation energy. On the one hand, it contains the difference between the real kinetic energy of the electrons and the approximated value; on the other hand, precise analytical form is not easy to write, all errors are included into the exchange-correlation energy because the Fermi quantum electronic systems must satisfy some quantum rules.
Based on the equations (2.15) and (2.16), we can further change the Lagrange multiplier \( \mu \) as

\[
\mu = \frac{\delta T[r]}{\delta \rho(r)} + V_{K_S}(r)
\]

\[
V_{K_S}(r) = V_{ext}(r) + V_C(r) + V_{xc}(r)
\]

where \( V_{K_S}(r) \) is the Kohn-Sham potential, \( V_{ext}(r) \) is the external Coulomb potential caused by the nuclei, the left ones are the Coulomb interaction between electrons and exchange-correlation potential

\[
\begin{align*}
V_C(r) &= \frac{\delta E_C[\rho(r)]}{\delta \rho(r)} = \frac{1}{2} \int \frac{\rho(r)\rho'(r)}{|r-r'|} dr dr' \\
V_{xc}(r) &= \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}
\end{align*}
\]

Finally, in order to complete the picture of single-electron states, we use \( N \) single-electron wavefunction to build the density function \( \psi_i(r) \)

\[
\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2
\]

and the kinetic energy of non-interaction electrons

\[
T_s[\rho(r)] = \sum_{i=1}^{N} \int \psi_i^*(r) \left( -\frac{\nabla^2}{2} \right) \psi_i(r) dr
\]

If we assume the variation of \( \rho(r) \) equal the one of \( \psi_i(r) \), and the Lagrange multipliers indicated by \( \varepsilon_i \), then we will have

\[
\delta \left[ E[\rho(r)] - \sum_{i=1}^{N} \varepsilon_i \left[ \int \psi_i^*(r) \psi_i(r) dr - 1 \right] \right] / \delta \psi_i(r) = 0
\]

Simply,
\[
\left[-\nabla^2 + V_{KS}(r)\right] \psi_i(r) = \varepsilon_i \psi_i(r)
\]  \hspace{1cm} (2.22)

Here equation (2.22) is the Kohn-Sham equation. We can get the charge density of ground state if the Kohn-Sham potential $V_{KS}(r)$ is known. But the Kohn-Sham potential itself $V_{KS}(r)$ also depends on the charge density $\rho(r)$. So, to solve the Kohn-Sham equations, we need to introduce the self-consistent iterative method.

### 2.1.3 Pseudopotential Method

To solve the Kohn-Sham equation (2.22), it is necessary to select one appropriate basis functions. There are a variety of basis functions for different systems[15-17]: Linear combination of atomic orbitals (LCAO), namely the tight binding approximation, linearized augmented plane wave (LAPW), Muffin-tin orbital linear combination method (LMTO), as well as Wannier function group and pseudopotential plane wave method.

One of the most convenient method is plane wave pseudopotential method, which VASP also based on because of its advantages: natural orthogonal; naturally compatible with periodic boundary conditions; do not vary as the atomic positions change; numerical implementation is relatively simple.

The external potential and the wave function of the ion core can be expanded using the plane wave function, but the region around the center of the ion core has a $1/r$ singularity because of the strong local potential. Thus, the wave function oscillate largely in the vicinity around the ion core; only in the middle region of two nuclei, the potential field changes slowly. Using a plane wave described the ground state of the innermost orbitas, the number would be huge, and the convergence will become very slow. But In
fact, the physics properties of the system typically depends on the behavior of valence electrons, weakly associated with the core electrons. For example, the electronic structures of the solid matter (metals, semiconductors, insulators) mainly depend on the electronic states near the Fermi level, but not the ion core. Pseudopotential approximation will ignore the core electrons, and replace the real interaction between electrons and nucleu with the weak ionic potential, meanwhile, the real wave function of valence electron will be instead by the pseudo-potential wave function. However, considering the area outside the core electrons ($r > r_c$), pseudopotential function will be consistent with the real wave function exactly, as shown in figure 2-1 [18].

![Figure 2-1: Pseudopotential method schematic, all-electronic (solid line) and pseudo-electrons (dashed line) potential and the corresponding wave function.](image)

For the solid multi-body system, the coordinate space can be divided into three different areas according to the characteristics of the wave function: the core area, region between
cores and the remaining areas. If we use $|\varphi_v\rangle$ and $|\varphi_c\rangle$ representing the wave function, and use $\varepsilon_v$ and $\varepsilon_c$ as the corresponding eigen-values, then we will get

$$\begin{align*}
H |\varphi_v\rangle &= \varepsilon_v |\varphi_v\rangle \\
H |\varphi_c\rangle &= \varepsilon_c |\varphi_c\rangle
\end{align*}$$

(2.23)

We also can build the new wave function

$$\begin{align*}
|\varphi_v\rangle &= |\varphi_v^{PS}\rangle + \sum_c \beta_c |\varphi_c\rangle \\
\beta_c &= -\langle \varphi_c | \varphi_v^{PS}\rangle
\end{align*}$$

(2.24)

Based on the equations above, the system Hamiltonian can be written as

$$\begin{align*}
\left[H + \sum_c (\varepsilon_v - \varepsilon_c) |\varphi_v\rangle \langle \varphi_v| \right] |\varphi_v^{PS}\rangle &= (T + U) |\varphi_v^{PS}\rangle = \varepsilon_v |\varphi_v^{PS}\rangle \\
U &= V + \sum_c (\varepsilon_v - \varepsilon_c) |\varphi_v\rangle \langle \varphi_c|
\end{align*}$$

(2.25)

where $U$ is the pseudopotential, $|\varphi_v^{PS}\rangle$ is the pseudo wave function. We conclude that some points from the equations above: the pseudo wave function and the wave function of valence electrons has the same eigen-value $\varepsilon_v$. Since $\varepsilon_v$ is larger than $\varepsilon_c$, so the second term in pseudopotential equation is the positive one, and the orthogonalization of pseudopotential brings a repulsive potential, which will compensate the real attraction potential and weaken the total potential. As a result, the pseudopotential assumption will make the potential in the core area relatively flat, which can be described using small number of plane waves, shown in schematic figure 1-1. There are many different types of pseudopotential, including local pseudopotential, ultrasoft (US) pseudopotential [19-21], projective argumented wave (PAW) pseudopotential [22-23], BSH pseudopotential [24] and norm-conserving pseudopotential [25-27].
2.2 VASP

VASP (Vienna Ab-initio Simulation Package) is a widely used program, based on the plane wave pseudopotential and density functional theory, and developed by George Kress and Jurgen Furthmuller [28-31]. VASP package also contains a set of optimized ultrasoft pseudopotentials and PAW pseudopotentials of all elements in periodic table. Through the self-consistent iterative method, VASP can solve Kohn-Sham equations under different density approximation. VASP package not only contains the local density approximation LDA, but also contains the following generalized gradient approximation: LM, BP, PW91, PBE, RPBE. To determine the electronic ground state of one system, the optimized CG method (Conjugate-gradient algorithm conjugate gradient method) was referred by Teter et al [32], and the Block Davidson scheme was initiated by Davidson, or a residual minimization method based on unconstrained matrix diagonalization scheme also can be used. After each optimized iteration, the charge density must be recalculated. Figure 2.2 shows the self-consistent iterative process of VASP package for calculating every electronic structure [33]. In order to ensure the numerical stability, a new density will mix with the old one of the last cycle, obeying the Pulay rule, then the improved charge density will become a new input density for the second round of circulation. In addition, VASP package will sample the numerical points from the K-space. There are several different schemes to choose: the Monkhorst-Pack scheme [34], the tetrahedral Blöch correction method [35], Fermi smearing method [33], Gaussian smearing method [36] and Methfessel-Paxton method [37].
VASP can precisely simulate the periodic atom structures and calculate several corresponding physics parameters, including the structural parameters (bond lengths, bond angles, lattice constants, atomic positions, etc.); equation of state and mechanical properties (elasticity modulus volume and elastic constants); electronic structure (energy levels, charge density, band, electronic density of states, etc.); and optical properties.
**Self-consistent Kohn–Sham equations**

1. **Initial guess**
   
   \[ n^\uparrow(r), n^\downarrow(r) \]

2. **Calculate effective potential**
   
   \[ V_{\text{eff}}^\sigma(r) = V_{\text{ext}}(r) + V_{\text{Hartree}}[n] + V_{\text{xc}}[n^\uparrow, n^\downarrow] \]

3. **Solve KS equation**
   
   \[ \left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}^\sigma(r)\right) \psi_i^\sigma(r) = \varepsilon_i^\sigma \psi_i^\sigma(r) \]

4. **Calculate electron density**
   
   \[ n^\sigma(r) = \sum_i f_i^\sigma |\psi_i^\sigma(r)|^2 \]

5. **Self-consistent?**

6. **Output quantities**
   
   Energy, forces, stresses, eigenvalues, 

---

**Figure 2-2:** The self-consistent iteration for calculating the wave function in VASP [33]
Chapter 3

Unique Properties of CH$_3$NH$_3$PbI$_3$ Perovskites

Organic and inorganic halide perovskites have recently shown remarkable performance, especially the high open circuit voltage ($V_{oc}$) and long electron-hole diffusion length. First-principle calculations show that CH$_3$NH$_3$PbI$_3$ halide perovskite solar cell materials have its unique properties. Approaches for intrinsic and extrinsic doping organic-inorganic CH$_3$NH$_3$PbI$_3$ are investigated by density-functional theory calculations. Our results reveal that unusual defect physics of intrinsic doping and $p$-type prediction of extrinsic doping. For intrinsic doping, defects with low formation energies create only shallow levels, whereas defects with deep levels have high formation energies, which partially explain the long electron-hole diffusion length and high $V_{oc}$. Furthermore, CH$_3$NH$_3$PbI$_3$ can exhibit an intrinsic conductivity from a good $p$-type to a good $n$-type depending on the growth conditions. The unusual defect properties can be attributed to the strong Pb lone-pair $s$ orbital and I $p$ orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbI$_3$. For extrinsic doping, $p$-type CH$_3$NH$_3$PbI$_3$ halide perovskites can be realized by incorporation of some Group-IA, -IB, or -VIA elements such as Na, K, Rb, Cu, and O at I-rich growth conditions. We further show that $n$-type CH$_3$NH$_3$PbI$_3$ halide
perovskites are more difficult to realize under the extrinsic doping due to the formation for neutral defects or compensation from intrinsic point defects.

3.1 Introduction

Organic-inorganic methylammounium triiodideplumbate CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$)-based halide perovskites have recently emerged as promising solar photovoltaic absorbers.[1, 38-48] MAPbI$_3$ perovskite exhibits extremely high optical absorption coefficient and long electron-hole diffusion lengths [4-6]. It has clearly demonstrated its potential for producing high-efficiency and low-cost thin-film solar cells. The record efficiency of small area MAPbI$_3$-based thin-film solar cells has increased to 20.1% [1] from less than 4% [38] in four years.

The properties of defects, especially point defects, in absorbers play a critical role on determining the electron-hole diffusion length and $V_{oc}$ of a solar cell. Defects that create deep levels usually act as Shockley-Read-Hall non-radiative recombination centers and are responsible for can shorten short minority carrier lifetime and thus low $V_{oc}$. The long electron-hole diffusion length and high ratio of $V_{oc}/E_g$ indicate that CH$_3$NH$_3$PbI$_3$-based perovskite must have unusual defect properties. On the other hand, the Shockley-Queisser limit[49] for single-junction solar cell based on an absorber with $E_g$ of 1.5 eV should be close to 30%. To further improve the efficiency of halide perovskite-based thin-film solar cells, it is crucial to investigate thermodynamic stability of CH$_3$NH$_3$PbI$_3$ and the formation mechanisms of the dominant intrinsic and extrinsic point defects.
Moreover, the current MAPbI$_3$ perovskite thin-film solar cell technology faces challenges for large scale commercialization, primarily due to the use of expensive and unstable hole transport material (HTM)—2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9’-spirobifluorene (spiro-OMeTAD)[43,44]. MAPbI$_3$ solar cells using non-spiro-OMeTAD HTM layers such as CuSCN[50,51], NiO[50], and CuI[52] or no HTM layers[53-56] have exhibited poorer performance than the cells using spiro-OMeTAD HTM layers. An alternative possible approach to achieve low-cost and stable hole transport layers is to dope MAPbI$_3$ $p$-type. Furthermore, if MAPbI$_3$ can be doped both $p$-type and $n$-type, $p$-$n$ junction based solar cell structures, which have been the case for most inorganic solar cells, may be realized. This could provide new opportunities for fabricating MAPbI$_3$ thin-film solar cells with improved efficiency and stability as compared to current MAPbI$_3$–based thin-film solar cells.

3.2 Method Details

The defect calculations were based on a (4×4×4) host supercell with the Γ point. The supercell contains 768 atoms. With this large supercell size, both conduction band maximum (VBM) and conduction band minimum (CBM) are folded to the Γ point. Our test calculations indicate that the use of (4×4×4) host supercell with the Γ point provides reliable results. The DFT calculations were performed using VASP code[28-31] with the standard frozen-core projector augmented-wave (PAW) method. The cut-off energy for basis functions was 400 eV. The general gradient approximation (GGA) was used for exchange-correlation[23, 57]. Atomic positions are relaxed until all the forces on atoms are below 0.05 eV/Å. The effect of spin-orbital coupling (SOC) in MAPbI$_3$ due to strong
relativistic effect of Pb has been discussed in literature[58-60]. However, the band gap errors of using GGA and non-SOC are cancelled with each other in occurrence[61]. Therefore, the GGA gives the experimental band gap without any underestimation. Because the use of large supercell size of 768 atoms makes calculations with SOC not possible, SOC was not considered in our calculations.

In formation energy calculations, the equilibrium growth condition of MAPbI$_3$ should be considered so that the chemical potentials of MA ($\mu$$_{\text{MA}}$), Pb ($\mu$$_{\text{Pb}}$), and I ($\mu$$_{\text{I}}$) satisfy the relation of $\mu$$_{\text{MA}}$ + $\mu$$_{\text{Pb}}$ + 3$\mu$$_{\text{I}}$ = $\Delta$H(MAPbI$_3$) = -5.26 eV . To exclude the possible secondary phases of PbI$_2$ and MAI (rock-salt phase), the chemical potentials of MA, Pb, and I ($\mu$$_{\text{MA}}$, $\mu$$_{\text{Pb}}$, and $\mu$$_{\text{I}}$) are constrained, which are related to growth conditions. In our defect calculations, we have considered three chemical potential combinations that are related to three representative growth conditions: I-rich/Pb-poor ($\mu$$_{\text{MA}}$ = -2.87 eV, $\mu$$_{\text{Pb}}$ = -2.39 eV, $\mu$$_{\text{I}}$ = 0 eV) moderate ($\mu$$_{\text{MA}}$ = -2.41 eV, $\mu$$_{\text{Pb}}$ = -1.06 eV, $\mu$$_{\text{I}}$ = -0.60 eV) and I-poor/Pb-rich ($\mu$$_{\text{MA}}$ = -1.68 eV, $\mu$$_{\text{Pb}}$ = 0 eV, $\mu$$_{\text{I}}$ = -1.19 eV). The details of these chemical points can be found in our publications.[6]

The calculation of transition energies and formation energies of defects followed the methods described in literature.[62,63] The chemical potentials of considered dopant elements must satisfy additional constraints to exclude the formation of dopant-related secondary phases. For example, for extrinsically doping using group-IA elements such as Na, K, and Rb, we exclude the possible secondary phases of NaI, KI, and RbI. Therefore, the following constrains must also be satisfied: $\mu$$_{\text{Na}}$ + $\mu$$_{\text{I}}$ < $\Delta$H(NaI) = -2.59 eV, $\mu$$_{\text{K}}$ + $\mu$$_{\text{I}}$ < $\Delta$H(KI) = -3.01 eV, and $\mu$$_{\text{Rb}}$ + $\mu$$_{\text{I}}$ < $\Delta$H(RbI) = -3.03 eV. Similar constrains are
considered for excluding the formation of other possible dopant-related secondary phases, for examples, CuI, SrI$_2$, BaI$_2$, SbI$_3$, BiI$_3$, PbO, PbS, PbSe, and PbTe.

### 3.3 Results and Discussion

#### 3.3.1 Intrinsic Doping

In perovskite CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$ and Pb donate one and two electrons, respectively, to three I ions, forming a direct band gap of 1.5 eV between unoccupied Pb $p$ orbital and occupied I $p$ orbital [see Figures 3-1(b) to 3-1(f)]. The CH$_3$NH$_3$ molecules do not make any significant contribution to the band edges [Fig. 3-1(d)] but donate one electron to Pb-I framework. It is noted that for a stable perovksite ABX$_3$, the bond length ratio $(r_A+r_X)/(r_B+r_X)$ is required to be close to 1 and thus the size of A atom is much larger than that of the B atom [34]. For CH$_3$NH$_3$PbI$_3$, Pb is already a large atom and it is difficult to find single element A that are large enough to stabilize APbI$_3$. Therefore, the large-size CH$_3$NH$_3$ molecules can effectively stabilize the perovskite structures. However, the CH$_3$NH$_3$ molecules do not make considerable contribution to the electronic structure of CH$_3$NH$_3$PbI$_3$. The conduction band minimum (CBM) of CH$_3$NH$_3$PbI$_3$ is mainly derived from Pb $p$ orbitals with negligible contribution from I, indicating a high ionicity of CH$_3$NH$_3$PbI$_3$ [Fig. 3-1(g)]. The fully-occupied $s$ orbitals of Pb have strong antibonding coupling [Fig. 3-1(h)] with I $p$ orbitals, making the upper valence bands (VBs) dispersive [Fig. -1(b)]. The band edge characters are consistent with recent investigations[35, 36]. The strong $s$-$p$ antibonding coupling results in small effective masses for both electrons and holes, making CH$_3$NH$_3$PbI$_3$-based perovskites the ideal candidates for thin-film solar cells with a $p$-$i$-$n$ configuration.
The chemical potentials of Pb and I satisfying the thermodynamic equilibrium growth conditions are shown as the red region in Figure 3-2. This narrow and long chemical range indicates the growth conditions for synthesizing CH$_3$NH$_3$PbI$_3$ phase in the equilibrium conditions. The small chemical range is in consistent with the calculated small dissociation energy of from CH$_3$NH$_3$PbI$_3$ to CH$_3$NH$_3$I and PbI$_2$, defined as $E(\text{CH}_3\text{NH}_3\text{I}) + E(\text{PbI}_2) - E(\text{CH}_3\text{NH}_3\text{PbI}_3)$, only 0.27 eV. The narrow but long chemical potential range indicates that the growth conditions should be carefully controlled to form the desirable CH$_3$NH$_3$PbI$_3$ perovskite phase.
Figure 3-2: Calculated chemical ranges for forming CH$_3$NH$_3$PbI$_3$ (middle red region), PbI$_2$ (upper right yellow region), and CH$_3$NH$_3$I (left region). Three representative points A($\mu_{\text{MA}} = -2.87$ eV, $\mu_{\text{Pb}} = -2.39$ eV, $\mu_{\text{I}} = 0$ eV), B($\mu_{\text{MA}} = -2.41$ eV, $\mu_{\text{Pb}} = -1.06$ eV, $\mu_{\text{I}} = -0.60$ eV), and C($\mu_{\text{MA}} = -1.68$ eV, $\mu_{\text{Pb}} = 0$ eV, $\mu_{\text{I}} = -1.19$ eV) were used for calculating the formation energies of point defects.[6]

We have considered all possible point defects including CH$_3$NH$_3$, Pb, and I vacancies ($V_{\text{MA}}$, $V_{\text{Pb}}$, $V_{\text{I}}$), CH$_3$NH$_3$, Pb and I interstitial ($\text{MA}_{\text{i}}$, $\text{Pb}_{\text{i}}$, $\text{I}_{\text{i}}$), CH$_3$NH$_3$ on Pb and Pb on CH$_3$NH$_3$ cation substitutions ($\text{MA}_{\text{Pb}}$, $\text{Pb}_{\text{MA}}$) and four antisite substitutions, CH$_3$NH$_3$ on I ($\text{MA}_{\text{i}}$), Pb on I ($\text{Pb}_{\text{i}}$), I on CH$_3$NH$_3$ ($\text{I}_{\text{MA}}$), and I on Pb ($\text{I}_{\text{Pb}}$). As the formation energies of point defects depend on the chemical potentials of the constituent element, we have chosen three representative points, A (I-rich/Pb-poor), B (moderate), C (I-poor/Pb-rich), in the chemical range shown in Figure 3-2 to study the defect properties. Their formation energies of the considered point defects as a function of Fermi level position at chemical
potential A, B, C are shown in Fig. 3-3(a), (b), and (c), respectively. It is seen that the conductivity of CH$_3$NH$_3$PbI$_3$ depends on the growth conditions. At chemical point A, i.e., I-rich/Pb-poor, CH$_3$NH$_3$PbI$_3$ should be intrinsically good $p$-type. At chemical point B, i.e., moderate, CH$_3$NH$_3$PbI$_3$ should be intrinsic (low conductivity). At chemical point C, i.e., I-poor/Pb-rich, CH$_3$NH$_3$PbI$_3$ should be intrinsically good $n$-type. Such flexible defect properties are distinguished from conventional thin-film solar cell absorbers such as CuInSe$_2$ (CIS)[9] and Cu$_2$ZnSnS$_4$ (CZTS)[10]. Donors in CIS and CZTS generally have much higher formation energies than acceptors. For example, the formation energies of donors Cu$_i$ and In$_{Cu}$ in CIS are more than 2 eV higher than that of acceptor V$_{Cu}$. Thus V$_{Cu}$ dominates the conductivity of CIS[9]. In CH$_3$NH$_3$PbI$_3$, the dominant donor MA$_i$ and dominant acceptor V$_{Pb}$ have comparable formation energies. The low formation energy of V$_{Pb}$ in CH$_3$NH$_3$PbI$_3$ is due to the energetically unfavorable $s$-$p$ antibonding coupling, which resembles the $p$-$d$ antibonding coupling in CIS[9]. The fully occupied antibonding state between Pb $s$ and I $p$ coupling does not gain electronic energy thus tend to bond break and form a vacancy. The lower formation energy of MA$_i$ could be explained by its weak van der Waals interaction with Pb-I framework.
Figure 3-3: Calculated formation energies of considered intrinsic point defects in CH$_3$NH$_3$PbI$_3$ as a function of Fermi level at three chemical potential points, (a) A, (b) B, and (c) C, shown in Figure 2. Defects with high formation energies are shown in dashed lines. [6]

The transition level of a defect is the Fermi level position where the defect can donate/accept electrons. Therefore, the defect with transition level deep in the band gap will attract electron/hole and act as Shockley-Read-Hall nonradiative recombination centers. The high performance of CIGS-based thin-film solar cell is partially attributed to its shallow dominant defects ($V_{Cu}$) with transition level only 0.03 eV above the VBM of CIGS[9]. In CZTS, the dominant defect ($Cu_{Zn}$) has a deeper transition level of 0.10 eV above the VBM of CZTS, which is considered as the possible reason for the low $V_{oc}$ of CZTS-based solar cells[10]. The calculated transition levels for all considered point defects in CH$_3$NH$_3$PbI$_3$ are shown in Figure 3-4 and summarized in Table 2.1. It is seen that the defects that have low formation energies, such as MA$_i$, $V_{Pb}$, MA$_{Pb}$, I$_i$, V$_i$, and $V_{MA}$, have transition energies less than 0.05 eV above (below) the VBM (CBM) of CH$_3$NH$_3$PbI$_3$. On the other hand, all the defects that create deep levels, such as I$_{Pb}$, I$_{MA}$,
Pb, PbI, have high formation energies. Because only the defects with deep levels are responsible for non-radiative recombination, these formation energies strongly indicate that CH₃NH₃PbI₃ should intrinsically have rather low nonradiative recombination rate, explaining the reported long electron-hole diffusion length. The reason why the dominant acceptors, Vₚb and MAₚb, are shallow is attributed to strong s-p antibonding states at the VBM of CH₃NH₃PbI₃. Without Pb s lone-pair orbitals, the VBM should be derived only from I p orbitals. The s-p antibonding coupling between Pb lone pair s and I p orbitals pushes the VBM up to a higher level so that the acceptors are generally shallower than in the case without strong s-p antibonding coupling. The mechanism resembles the shallow VₐCu in CIS, where the VBM has antibonding states formed by Cu d and Se p orbitals. The shallow nature of dominant donors, MAi and Vi, is due to the high ionicity of CH₃NH₃PbI₃. As discussed above, the large-size MA molecules help stabilize the perovskite structure and donate electrons to the 3D Pb-I framework for charge balance. The MAi has no covalent bonding with Pb-I framework and does not create additional gap states. As shown in Fig. 3-1(e), the CBM of CH₃NH₃PbI₃ is mostly contributed from Pb p orbital exhibiting very weak covalent bonding between P and I [Fig. 3-1(h)]. Our previous study has shown that weak covalent bonding generally leads to the shallow vacancy levels.
Table 3.1. Calculated formation energies (unit: eV) of twelve neutral defects in CH$_3$NH$_3$PbI$_3$ at chemical potential points A, B, and C, shown in Figure 2.

<table>
<thead>
<tr>
<th></th>
<th>$I_i$</th>
<th>$\text{MA}_{\text{Pb}}$</th>
<th>$V_{\text{MA}}$</th>
<th>$V_{\text{Pb}}$</th>
<th>$I_{\text{MA}}$</th>
<th>$I_{\text{Pb}}$</th>
<th>$\text{MA}_{\text{Pb}}$</th>
<th>$V_{\text{MA}}$</th>
<th>$V_{\text{Pb}}$</th>
<th>$I_{\text{MA}}$</th>
<th>$I_{\text{Pb}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.23</td>
<td>0.28</td>
<td>0.81</td>
<td>0.29</td>
<td>1.96</td>
<td>1.53</td>
<td>1.39</td>
<td>2.93</td>
<td>1.87</td>
<td>4.24</td>
<td>3.31</td>
</tr>
<tr>
<td>B</td>
<td>0.83</td>
<td>1.15</td>
<td>1.28</td>
<td>0.93</td>
<td>1.62</td>
<td>3.01</td>
<td>3.45</td>
<td>2.51</td>
<td>1.27</td>
<td>2.91</td>
<td>2.25</td>
</tr>
<tr>
<td>C</td>
<td>1.42</td>
<td>1.47</td>
<td>2.01</td>
<td>2.68</td>
<td>4.34</td>
<td>5.10</td>
<td>0.20</td>
<td>1.74</td>
<td>0.67</td>
<td>1.85</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 3-4: Calculated transition energy levels of donor and acceptor defects in CH$_3$NH$_3$PbI$_3$.\textsuperscript{50}

3.3.2 Extrinsic Doping

Because of the use of large supercell, the calculations of defects are very time demanding. In this paper, we have only considered the dopants that introduce singly charged defect states, because defects with multiple charges usually produce deep levels. Furthermore, dopants that have significant size mismatch with the substituting elements
were not considered. We have considered group-IA and -IB elements including K, Na, Rb, and Cu on interstitial sites (Na$_{i}$, K$_{i}$, Rb$_{i}$, and Cu$_{i}$) as donors and on Pb sites (Na$_{Pb}$, K$_{Pb}$, Rb$_{Pb}$, and Cu$_{Pb}$) as acceptors. We have considered group-IIA and -IIB elements including Sr, Ba, Zn, and Cd on MA site (Sr$_{MA}$, Ba$_{MA}$, Zn$_{MA}$, and Cd$_{MA}$) as donors and on Pb site (Sr$_{Pb}$, Ba$_{Pb}$, Zn$_{Pb}$, and Cd$_{Pb}$) as neutral defects. We have considered group-IIIA elements, Al, Ga, and In, and group VA elements, Sb and Bi, on Pb sites (Al$_{Pb}$, Ga$_{Pb}$, In$_{Pb}$, Sb$_{Pb}$, and Bi$_{Pb}$) as potential donors. We have considered O, S, Se, and Te on I sites (O$_{I}$, S$_{I}$, Se$_{I}$, and Te$_{I}$) as potential acceptors.

![Conduction Bands and Valence Bands](image)

**Figure 3-5:** Calculated transition energy levels of identified shallow donors and shallow acceptors.

The calculated transition energy levels of identified shallow donors are shown in Figure 3-5. The transition energy levels are referenced to the CBM of CH$_3$NH$_3$PbI$_3$. It shows that interstitial group-IA and -IB elements, Na$_{i}$, K$_{i}$, Rb$_{i}$, and Cu$_{i}$, are shallow donors. Group-IIA elements such as Sr and Ba at MA sites are also shallow donors. They are neutral defects when they occupy Pb sites. Our calculations revealed that Zn$_{MA}$, Cd$_{MA}$, Al$_{Pb}$, Ga$_{Pb}$, and In$_{Pb}$ are deep donors. Therefore, these dopants will not be
considered further in this paper. Bi\textsubscript{Pb} and Sb\textsubscript{Pb} are shallow donors with transition energy levels of 0.17 eV and 0.19 eV, respectively.

The calculated transition energy levels of the identified shallow acceptors are shown in Figure 3-6. The transition energy levels are referenced to the VBM of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}. The calculated transition energy levels of Na\textsubscript{Pb}, K\textsubscript{Pb}, Rb\textsubscript{Pb}, and Cu\textsubscript{Pb} are -0.026 eV, 0.014 eV, 0.020 eV, and 0.084 eV, respectively. The calculated transition energy levels for O\textsubscript{I}, S\textsubscript{I}, Se\textsubscript{I}, and Te\textsubscript{I} are -0.076 eV, 0.021 eV, 0.070 eV, and 0.128 eV, respectively. The negative transition energies for Na\textsubscript{Pb} and O\textsubscript{I} mean that their levels are below the VBM, indicating spontaneous ionizations.

![Fig. 3-6: Calculated formations energies of defects formed by group-IA and -IB elements as functions as the Fermi levels at (a) I-rich/Pb-poor (Fig3-2: A point) and (c) I-poor/Pb-rich conditions.](image-url)
rich (Fig3-2: C point) conditions. The intrinsic defects with the lowest formation energies are shown as the dashed line. The vertical dotted lines indicate the Fermi level pinning.

While the calculated transition energy levels show that many of the considered dopants produce shallow donors and acceptors, the extrinsic doping properties of MAPbI₃ rely on the positions of Fermi levels, which are determined by the formation of all defects including intrinsic and extrinsic defects. To evaluate the extrinsic doping properties of MAPbI₃, we have calculated the formation energies of the above-preselected dopants with shallow transition energies under two representative growth conditions: I-rich/Pb-poor and I-poor/Pb-rich, indicated by A, C points in Figure 3-2.

**Fig. 3-7:** The calculated formation energies as functions of Fermi levels for group-IIA at (a) I-rich/Pb-poor (Fig3-2: A point) and (c) I-poor/Pb-rich (Fig3-2: C point), showing that the formation energies of Sr$_{\text{MA}}$ and Ba$_{\text{MA}}$ are generally higher than that of Sr$_{\text{Pb}}$ and Ba$_{\text{Pb}}$, and intrinsic defects V$_{\text{Pb}}$ (Pb vacancy) and MA$_{\text{i}}$. 
The calculated formation energies as functions of Fermi levels for group-IIA at I-rich/Pb-poor and I-poor/Pb-rich show that the formation energies of Sr\textsubscript{MA} and Ba\textsubscript{MA} are generally higher than that of Sr\textsubscript{Pb} and Ba\textsubscript{Pb}, and intrinsic defects V\textsubscript{Pb} (Pb vacancy) and MA\textsubscript{i} (Fig. 3-7). This is mainly due to the special electronic properties of MAPbI\textsubscript{3}. It is known that the fully-occupied s orbital of Pb\textsuperscript{2+} has strong antibonding coupling with I p orbital. The s-p antibonding coupling is energetically unfavorable.\textsuperscript{30,41,42} When a Pb is substituted by a Sr\textsuperscript{2+} or Ba\textsuperscript{2+} that does not have fully occupied s orbital, the energetically unfavorable s-p antibonding coupling is eliminated, leading to energetically favorable substitutions. Therefore group-IIA elements are not expected to produce better n-type MAPbI\textsubscript{3} than intrinsic defects though these dopants can produce very shallow donor levels.
The doping using Sb and Bi at I-rich/Pb-poor condition is strongly compensated by the formation of $V_{\text{Pb}}$ as shown in Fig. 3-8. The Fermi levels are pinned at 0.16 eV and 0.19 eV above the VBM, respectively for Sb and Bi doping. Therefore, Sb and Bi doping at I-rich/Pb-poor conditions cannot lead to $n$-type MAPbI$_3$. At I-poor/Pb-rich condition, the Fermi level is pinned by the intrinsic defects, $\text{MA}_i$ and $V_{\text{Pb}}$. Therefore, Sb and Bi doping is not expected to produce better $n$-type MAPbI$_3$ than the intrinsic $n$-type.
Figure 3-9: Calculated formations energies of defects formed by group-VI elements as functions as the Fermi levels at (a) I-rich/Pb-poor (Fig3-2: A point) and (c) I-poor/Pb-rich (Fig3-2: C point).

Figure 3-9 reveals the calculated formation energies as functions of Fermi levels for group-VIA elements on I sites at I-rich/Pb-poor and I-poor/Pb-rich conditions, respectively. The chemical potentials for O, S, Se, and Te are constrained to avoid the formation of secondary phases of PbO, PbS, PbSe, and PbTe. The calculated formation enthalpies are -2.96 eV, -1.16 eV, -1.25eV and -0.96eV for PbO, PbS, PbSe, and PbTe, respectively. The dashed lines show the intrinsic defects with the lowest formation energies. At I-rich/Pb-poor growth condition (Fig. 3-9), the doping of O$_i$ is pinned by MA$_i$ at the VBM. An interstitial O atom binds to two H atoms of a MA molecule. Like O in Si, O interstitials in MAPbI$_3$ do not produce any gap states and therefore are neutral.
defects. The results suggest that doping with O should lead to better $p$-type MAPbI$_3$ than the doping of intrinsic defects at I-rich/Pb-poor conditions. However, for S, Se, and Te doping, the formation energies of S$_{I}$, Se$_{I}$, and Te$_{I}$ are much higher than the formation energy of intrinsic acceptor, V$_{Pb}$. Therefore, the $p$-type conductivity will be determined by the intrinsic defects. At I-poor/Pb-rich condition, the doping is strongly compensated by the formation of intrinsic point defects. Therefore, doping using group-VIA elements leads to $p$-type MAPbI$_3$ at I-rich/Pb-poor growth condition, but $n$-type at I-poor/Pb-rich condition.

**Fig. 3-10:** Calculated total DOS and partial DOS from acceptors of O$_{I}$, S$_{I}$, Se$_{I}$, and Te$_{I}$. The DOS of the acceptors are enlarged by 500 times.
Our calculated total density of states (DOS) and partial DOS (Fig. 3-10) from group-VIA acceptors of O, S, Se, and Te support the above conclusion that O should lead to better p-type type MAPbI$_3$ than other group-VIA elements. It is seen clearly that the O $p$ state is very delocalized with strong coupling to the valence band of MAPbI$_3$. However, the $p$ states of S, Se, and Te show clear narrow peaks, indicating strong localization. The trend is consistent with the trend of the energy position of the atomic $p$-orbitals of the O, S, Se, and Te.

### 3.4 Conclusion

In conclusion of the intrinsic doping, our calculations have shown that CH$_3$NH$_3$PbI$_3$ exhibits unusual defect physics that are superior for solar photovoltaic applications: Defects with low formation energies create only shallow levels, whereas defects with deep levels have high formation energies. The conductivity of CH$_3$NH$_3$PbI$_3$ can tuned from being $n$-type to intrinsic and to $p$-type by controlling the growth conditions. The unusual defect properties were found to be due to the strong Pb lone-pair $s$ orbital and I $p$ orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbI$_3$. Our results suggest that careful control of the growth condition is the key to realize high efficiency thin-film solar cells based on halide perovskite absorbers.

We have studied the doping properties of MAPbI$_3$ perovskite with extrinsic dopants including group-IA, -IB, -IIA, -IIB, -IIA, -VA, and –VIA elements. We found that show that MAPbI$_3$ perovskite may be doped more easily $p$-type than $n$-type by extrinsic dopants. Our results suggest that good p-type MAPbI$_3$ may be produced by
doping with external elements including Na, K, Rb, Cu and O at I-rich/Pb-poor growth conditions. Group-IIA elements such as Sr and Ba and group-VA elements such as Sb and Bi can produce shallow donor levels, but they cannot lead to good $n$-type MAPbI$_3$ due to the formation for neutral defects and compensation from intrinsic point defects. Our results imply that non-equilibrium growth conditions may be needed to dope MAPbI$_3$ for good $n$-type conductivities.
Chapter 4

Tuning the Photovoltaic Properties of CH$_3$NH$_3$PbBr$_3$ Perovskite Solar Cell Absorber via Defect Engineering

Through density-functional theory calculation, we show that despite a large band gap of 2.2 eV, the dominant defects in CH$_3$NH$_3$PbBr$_3$ create only shallow levels. These unusual defect properties are largely due to the strong Pb lone-pair $s$ orbital and Br $p$ orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbBr$_3$. We further show that the photovoltaic properties of CH$_3$NH$_3$PbBr$_3$–based perovskite absorbers can be tuned via defect engineering. CH$_3$NH$_3$PbBr$_3$ with low carrier concentration, i.e., required for good solar cell absorbers, can be grown under moderate growth conditions. Highly conductive p-type CH$_3$NH$_3$PbBr$_3$ can be synthesized under Br-rich growth conditions. Such CH$_3$NH$_3$PbBr$_3$ may be potential low-cost hole transporting materials for lead halide perovskite solar cells. Under thermal equilibrium growth conditions, extrinsic doping is found to be ineffective for manipulating the electric properties of CH$_3$NH$_3$PbBr$_3$. Good n-type CH$_3$NH$_3$PbBr$_3$ should be produced through post-deposition diffusion of alkaline or alkaline earth metal ions.

4.1 Introduction
Multijunction solar cell technology is so far the only technology that has demonstrated efficiencies higher than the Shockley-Queisser limit for solar to electricity conversion efficiency [64,65]. High efficiency tandem cells based on polycrystalline thin film semiconductors posses the most potential for producing low-cost solar electricity. However, up to now, high efficiency tandem cells have only been achieved with epitaxial grown single-crystal inorganic semiconductors, such as GaAs and GaInP based semiconductors [64]. High efficiency tandem cells based on polycrystalline thin films are still not available. The biggest challenge is to produce high efficiency and high open circuit voltage ($V_{OC}$) top cells. For top cells, the absorbers should have band gaps around 1.8 eV [66]. CuGaSe$_2$, Cd$_{1-x}$Zn$_x$Te, and CdSe are suitable for top cells. However, polycrystalline thin-film solar cells based on these absorbers have shown poor $V_{OC}$’s [38, 67-68], largely due to the non-radiative recombination caused by defects with deep levels. This situation may soon be changed by lead halide perovskites CH$_3$NH$_3$PbX$_3$ (X = I, Cl, Br)-based organic-inorganic thin film solar cells. In less than five years, the reported efficiency of lead halide perovskite-based thin film solar cells has improved quickly, from 3.8% in 2009 to 20.1% in 2014 [1, 3-4, 38-48, 56, 69]. Remarkably, CH$_3$NH$_3$PbX$_3$ perovskites have very long electron and hole carrier diffusion lengths. As a result, the cells have demonstrated a record $V_{OC}$ of 1.13 V. Beside the exceptional high efficiency and $V_{OC}$, lead halide perovskites are also capable of band gap tuning from about 1.5 (CH$_3$NH$_3$PbI$_3$) to 2.2 eV (CH$_3$NH$_3$PbBr$_3$) by changing the compositions of perovskites. This capability makes lead halide perovskites ideal candidates for all perovskite thin-film tandem cell applications.
\( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) has a band gap of about 2.2 eV and is a suitable candidate for the top cells of all perovskite tandem cells. Recent reports have shown that high \( V_{OC} \)’s can be realized with solar cells using \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \)-based perovskite absorbers. For example, Edri et al. have achieved a ~1.3 V \( V_{OC} \) for a \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \)-based solar cell and a ~1.5 V \( V_{OC} \) for a \( \text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{Cl}_x \) based solar cell [70,71]. Seok et al. have also reported a \( V_{OC} \) of 1.4 V for \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \) based thin-film cells [72]. Zhao and Zhu have recently achieved 10% efficiency cells based on a \( \text{CH}_3\text{NH}_3\text{PbI}_2\text{Br} \) perovskite absorbers with a band gap of 1.8 eV[73]. Therefore, \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \)-based absorbers show clearly the potential for achieving high efficiency and high \( V_{OC} \) top cells. The \( V_{OC} \) of a thin-film solar cell is typically determined by the non-radiative recombination in the absorber layer and at interfaces. To further improve the \( V_{OC} \)’s and efficiencies for \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \)-based solar cells, it is important to understand defect properties and tune the photovoltaic properties of \( \text{CH}_3\text{NH}_3\text{PbBr}_3 \)-based absorbers.

### 4.2 Method Details

The DFT calculations were performed using VASP code with the standard frozen-core projector augmented-wave (PAW) method [22, 30]. The cut-off energy for basis functions was 400 eV. The general gradient approximation (GGA) was used for exchange-correlation [23, 57]. Atomic positions are relaxed since all the forces on atoms are below 0.05 eV/Å. The effect of SOC was previously reported in \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) due to strong relativistic effect of Pb [58-60, 74]. However, the band gap errors of using GGA and non-SOC are cancelled with each other in occurrence for \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) [61]. Our previous results and recent report from other groups have shown that non-SOC GGA...
calculations give reasonably good results for electronic, optical, and effect properties in CH$_3$NH$_3$PbI$_3$ [6]. For CH$_3$NH$_3$PbBr$_3$, our calculated band gap using non-SOC and GGA is about 1.89 eV, which is about 0.31 eV smaller than the experimental value. Furthermore, DFT calculations using SOC and GGA significantly underestimate the band gaps of lead halide perovskites. To produce the correct band gaps, SOC plus hybrid functional (HSE06) must be used. However, calculations using SOC plus HSE is very computation time demanding. For defect calculations, we find that a large supercell size of (4×4×4) is required to obtain reliable results. This makes calculations using SOC plus HSE not feasible. Therefore, in this work, SOC and HSE are only used for examining the band structure and density of states (DOS) of CH$_3$NH$_3$PbBr$_3$. For defect calculations, non SOC and GGA are used based on a (4×4×4) supercell with the Γ point. Results reported by other groups have also shown that non SOC plus GGA describe well the defect properties of lead halide perovskites [75, 76, 80].

The chemical potentials of considered dopant elements must satisfy additional constrains to exclude the formation of dopant-related secondary phases. For example, for doping using group IA elements such as Na, K, and Rb, we exclude the possible secondary phases of NaBr, KBr, and RbBr. Therefore, the following constrains must also be satisfied: $\mu_{\text{Na}} + \mu_{\text{Br}} < \Delta H(\text{NaBr}) = -3.213$ eV, $\mu_{\text{K}} + \mu_{\text{Br}} < \Delta H(\text{KBr}) = -3.555$ eV, and $\mu_{\text{Rb}} + \mu_{\text{Br}} < \Delta H(\text{RbBr}) = -3.587$ eV. Similar constrains are considered for excluding the formation of other possible dopant-related secondary phases, for examples, CuBr, SrBr$_2$, BaBr$_2$, SbBr$_3$, BiBr$_3$, PbO, PbS, PbSe, and PbTe.

### 4.3 Results and Discussion
We investigate defect physics of CH$_3$NH$_3$PbBr$_3$ by density-functional theory (DFT) calculations. We compare them with the defect properties in CH$_3$NH$_3$PbI$_3$, which has a lower band gap. We find that in spite of the large band gap of 2.2 eV, the dominant defects in CH$_3$NH$_3$PbBr$_3$ create only shallow levels, which partially explain the high $V_{OC}$’s of CH$_3$NH$_3$PbBr$_3$-based solar cells. These unusual defect properties are attributed to the strong Pb lone-pair $s$ orbital and Br $p$ orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbBr$_3$. We further show that the photovoltaic properties of CH$_3$NH$_3$PbBr$_3$–based perovskite absorbers can be tuned via defect engineering. Under moderate growth conditions, CH$_3$NH$_3$PbBr$_3$ with low carrier concentration can be synthesized. Such CH$_3$NH$_3$PbBr$_3$ layers are optimal for being used as the absorbers. Under Br-rich/Pb-poor growth conditions, high concentration of shallow acceptor defects such as Pb and CH$_3$NH$_3$ vacancies is expected to form and produce highly conductive p-type CH$_3$NH$_3$PbBr$_3$, which can be used to replace the unstable and expensive hole transporting material, (HTM)—2,2’,7,7’-tetrakis-(N,N-di-p-methoxyphenylamine)9,9’-spirobifluorene (spiro-OMeTAD). Extrinsic doping is found not be able to produce better p-type or n-type conductivities than intrinsic doping. Good n-type CH$_3$NH$_3$PbBr$_3$ should be produced through post-deposition diffusion of alkaline or alkaline earth metal ions.

We first compare the electronic properties CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ with the cubic perovskite ABX$_3$ structure [45, 77-79]. We find that CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ have similar electronic properties, but they do exhibit some differences beside the band gap difference (1.5 eV for CH$_3$NH$_3$PbI$_3$ and 1.89 eV for CH$_3$NH$_3$PbBr$_3$). The calculated non spin-orbital coupling (SOC) PBE band structures for CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ are shown in Figs. 4-1(a) and 4-1(b), respectively. The overall
features look similar. In both cases, CH$_3$NH$_3$ molecules do not make considerable contribution to the electronic structures. The conduction band minima (CBMs) are mainly derived from Pb $p$ orbitals with negligible contribution from the halogen $p$ orbitals, indicating a high ionicity. The CBMs have very similar curvatures, suggesting similar effective masses for electrons. The fully-occupied $s$ orbitals of Pb have strong antibonding coupling between I $p$ or Br $p$ orbitals, making the upper valence bands (VBs) dispersive for both CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$, which lead to small effective masses for holes. Some differences are observed on the upper VBs: the upper VB is wider for CH$_3$NH$_3$PbBr$_3$ than for CH$_3$NH$_3$PbI$_3$. Because the upper VBs are due to the antibonding coupling between Pb lone pair $s$ orbitals and halogen $p$ orbitals, the wider upper VB indicates a strong $s$-$p$ antibonding coupling. This difference could be explained by the different ionic sizes of I$^{1-}$ (2.06Å) and Br$^{1-}$ (1.82Å). Because Br$^{1-}$ ions are smaller than I$^{1-}$ ions, the calculated lattice constant is 5.99Å for CH$_3$NH$_3$PbBr$_3$, but 6.39Å for CH$_3$NH$_3$PbI$_3$. The Pb-Br bond length is 3.04 / 2.97Å, which is 0.21Å smaller than the Pb-I bond length (3.25 / 3.15Å). Meanwhile, Br 4$p$ orbital is lower in energy than I 5$p$ and thus more close to Pb $s$ orbital. The short Pb-Br bond length and closer atomic orbitals should result in a stronger $s$-$p$ antibonding coupling. The strong $s$-$p$ antibonding coupling is expected to lead to a slightly more reduced effective mass for holes [5].
Figure 4-1: Calculated non SOC PBE band structures for (a) CH$_3$NH$_3$PbI$_3$ and (b) CH$_3$NH$_3$PbBr$_3$.

In thermodynamic equilibrium growth conditions, the existence of CH$_3$NH$_3$PbBr$_3$ should satisfy [62, 63]

$$\mu_{\text{CH}_3\text{NH}_3} + \mu_{\text{Pb}} + 3\mu_{\text{Br}} = \Delta H(\text{CH}_3\text{NH}_3\text{PbBr}_3) = -6.55eV$$

where $\mu_i$ is the chemical potential of the constitute element referred to its most stable phase and $\Delta H(\text{CH}_3\text{NH}_3\text{PbBr}_3)$ is the formation enthalpy of CH$_3$NH$_3$PbBr$_3$. For CH$_3$NH$_3$, we choose body-centered-cubic phase of CH$_3$NH$_3$ following Cs. To exclude the possible secondary phases of PbBr$_2$ and CH$_3$NH$_3$Br (rock-salt phase), the following constrains must also be satisfied.

$$\mu_{\text{CH}_3\text{NH}_3} + \mu_{\text{Br}} < \Delta H(\text{CH}_3\text{NH}_3\text{Br}) = -3.57eV$$

$$\mu_{\text{Pb}} + 2\mu_{\text{Br}} < \Delta H(\text{PbBr}_2) = -2.83eV$$
The chemical potentials of Pb and Br satisfying eqs (1) (2) (3) are shown as the orange region in Figure 4-2. This narrow and long chemical range indicates the growth conditions for synthesizing CH$_3$NH$_3$PbBr$_3$ phase in the equilibrium conditions. The small chemical range is consistent with the calculated small dissociation energy of from CH$_3$NH$_3$PbBr$_3$ to CH$_3$NH$_3$Br and PbBr$_2$, defined as $E(CH_3NH_3Br) + E(PbBr_2) - E(CH_3NH_3PbB_3)$, only 0.19 eV. The narrow but long chemical potential range also indicates that the growth conditions should be carefully controlled to form the desirable CH$_3$NH$_3$PbBr$_3$ perovskite phase. This situation is very similar to that seen in CH$_3$NH$_3$PbI$_3$.

**Figure 4-2:** Calculated chemical ranges for forming CH$_3$NH$_3$PbBr$_3$ (middle red region), PbI$_2$ (upper right blue region), and CH$_3$NH$_3$I (left region). Three representative points A ($\mu_{MA} = -3.57$ eV, $\mu_{Pb} = -2.99$ eV, $\mu_{Br} = 0$ eV), B ($\mu_{MA} = -2.95$ eV, $\mu_{Pb} = -1.48$ eV, $\mu_{Br} = -0.71$ eV), and C ($\mu_{MA} = -2.07$ eV, $\mu_{Pb} = 0$ eV, $\mu_{Br} = -1.49$ eV) were used for calculating the formation energies of point defects.
We have considered all possible point defects including CH$_3$NH$_3$ (MA), Pb, and Br vacancies ($V_{MA}$, $V_{Pb}$, $V_{Br}$), CH$_3$NH$_3$, Pb and I interstitial ($MA_i$, $Pb_i$, $Br_i$), CH$_3$NH$_3$ on Pb and Pb on CH$_3$NH$_3$ cation substitutions (MA$_{Pb}$, Pb$_{MA}$) and four antisite substitutions, CH$_3$NH$_3$ on Br ($MA_{Br}$), Pb on Br (Pb$_{Br}$), Br on CH$_3$NH$_3$ ($Br_{MA}$), and Br on Pb (I$_{Pb}$). We have first calculated the transition energies for these intrinsic defects, shown in Figure 4-3. The details for calculation can be found elsewhere [62, 63]. The donor like defects are shown at the left and the acceptor like defects are at the right side. It is seen that there are only four defects, i.e., Pb$_i$, Pb$_{Br}$, Br$_{MA}$, and Br$_{Pb}$, that produce deep levels in the band gap of CH$_3$NH$_3$PbBr$_3$. All other defects create only shallow levels. MA$_i$, Pb$_{MA}$, $V_{Br}$, and MA$_{Br}$ are shallow donors, whereas $Br_i$, MA$_{Pb}$, $V_{MA}$, and $V_{Pb}$ are shallow acceptors. The trend is very similar to that of intrinsic defects observed in CH$_3$NH$_3$PbI$_3$. It is noted that various atomic structures have been proposed for Pb$_i$ and I interstitials in CH$_3$NH$_3$PbI$_3$ by others [6, 75, 76]. We have tested all the structures and have considered the configuration with the lowest energies.

**Figure 4-3.** Calculated transition energy levels of intrinsic point defects in CH$_3$NH$_3$PbBr$_3$. 

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Defects that create deep levels are typically non-radiative recombination centers and therefore are detrimental to solar cell performance. For absorbers resulting in high \( V_{OC} \) and high efficiency solar cells, such defects must not be the dominant ones. To understand whether or not the above-mentioned four defects with deep levels are dominant defects in CH\(_3\)NH\(_3\)PbBr\(_3\), we have calculated the formation energies of the above considered defects. As the formation energies of point defects depend on the chemical potentials of the constituent elements, we have chosen chemical potentials following three representative points, A (Br-rich/Pb-poor), B (moderate), C (Br-poor/Pb-rich), in the chemical range shown in Figure 4-2 to study the defect properties. Figure 4-4 shows the calculated formation energies for the charge neutral defects as a function of chemical potential. The four defects that create deep levels are indicated by the solid lines. It is seen that these four defects are not the dominant defects, regardless of chemical potentials. Therefore, under thermal equilibrium growth conditions, CH\(_3\)NH\(_3\)PbBr\(_3\) is expected to exhibit very low concentration of deep level defects and therefore a low non-radiative recombination rate. This explains partially why despite a large band gap of 2.2 eV, CH\(_3\)NH\(_3\)PbBr\(_3\)-based solar cells are able to achieve high \( V_{OC} \)'s. The underlying physics are similar to that seen in CH\(_3\)NH\(_3\)PbI\(_3\): the strong antibonding coupling between Pb lone-pair \( s \) orbitals and Br \( p \) orbitals plays an important role. The antibonding coupling promotes the preferable formation of \( V_{Pb} \) and \( V_{Br} \), which are shallow defects. At chemical potential point A (Br-rich/Pb-poor) and point B (moderate), the dominant defects are \( V_{Pb} \), \( V_{MA} \), and Br\(_i\). These defects are all very shallow acceptors, indicating that CH\(_3\)NH\(_3\)PbBr\(_3\) films grown under these conditions are likely to be p-type. At chemical potential point C, the dominant defects are \( V_{Br} \), \( V_{Pb} \), Br\(_i\), and Pb\(_{MA} \). While
V_{Pb} and Br_{1} are shallow acceptors, V_{Br} and Pb_{MA} are shallow donors. Therefore, CH_{3}NH_{3}PbBr_{3} films grown under these conditions could be heavily compensated.

**Figure 4-4:** Calculated formation energies of intrinsic defects as a function of chemical potentials.

The electrical conductivity of a semiconductor is determined by the formation and compensations of charged defects. The formation energy of a charged defect depends on both the chemical potential and the Fermi level position of the system. We have therefore calculated formation energies of the above considered point defects as a function of Fermi level position at chemical potential points A, B, and C. The results are shown in Figures 4-5 (a), (b), and (c), respectively. It is seen that the conductivity of CH_{3}NH_{3}PbBr_{3} depends on the growth conditions. At chemical potential point A, i.e., Br-rich/Pb-poor, the Fermi level is determined by the formation of V_{Pb} and it is inside the VB. This indicates that CH_{3}NH_{3}PbBr_{3} grown under this condition should exhibit excellent p-type
conductivity. The conductivity is expected to be better than the intrinsic p-type conductivity of CH$_3$NH$_3$PbI$_3$. At chemical potential point B, i.e., a moderate growth condition, the Fermi level is pinned at 0.25 eV above the VBM by V$_{Br}$ and V$_{Pb}$. In this case, the CH$_3$NH$_3$PbBr$_3$ should still be just moderate p-type. At chemical potential point C, i.e., Br-poor/Pb-rich, CH$_3$NH$_3$PbBr$_3$ should be intrinsic or slightly n-type, as the Fermi level is pined at 1.07 eV by V$_{Br}$ and V$_{MA}$. Therefore, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ are expected to exhibit different electric properties. Under Pb-poor conditions, CH$_3$NH$_3$PbBr$_3$ is expected to be a better p-type than CH$_3$NH$_3$PbI$_3$. CH$_3$NH$_3$PbBr$_3$ may be used to replace spiro-OMeTAD as hole transport material for lead halide perovskite solar cells. However, CH$_3$NH$_3$PbBr$_3$ will be more difficult to exhibit n-type than CH$_3$NH$_3$PbI$_3$.

It has been shown[6] that the n-type conductivity of CH$_3$NH$_3$PbI$_3$ is due to the low formation of MA$_i$. However, it is found that the formation energy of MA$_i$ is too high to make CH$_3$NH$_3$PbBr$_3$ n-type. The higher formation energy of MA$_i$ in CH$_3$NH$_3$PbBr$_3$ is due to its smaller lattice constant compared to CH$_3$NH$_3$PbI$_3$. The low formation energies of V$_{Pb}$ in both CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ are due to the energetically unfavorable $s$-$p$ antibonding coupling, which resembles the $p$-$d$ anti-bonding coupling in CuInSe$_2$ [9]. The fully occupied antibonding between Pb $s$ and I $p$ /Br $p$ coupling does not gain electronic energy thus tend to bond break and form Pb and Br vacancies.
Figure 4-5: Calculated formation energies of considered intrinsic point defects in CH$_3$NH$_3$PbBr$_3$ as a function of Fermi level at three chemical potential points, (a) A, (b) B, and (c) C, shown in Figure 2. Defects with high formation energies are shown in dashed lines.

The electrical properties of semiconductors can be changed through extrinsic doping. We have further examined whether or not better p-type or n-type CH$_3$NH$_3$PbBr$_3$ can realized through extrinsic doping. We have considered the dopants that may introduce singly charged defect states, because defects with multiple charges usually produce deep levels. We have considered group IA and IB elements including K, Na, Rb, and Cu on interstitial sites (Na$_i$, K$_i$, Rb$_i$, and Cu$_i$) as donors and on Pb sites (Na$_{Pb}$, K$_{Pb}$, Rb$_{Pb}$, and Cu$_{Pb}$) as acceptors. We have considered group-IIA and IIB elements including Sr, Ba, Zn, and Cd on MA site (Sr$_{MA}$, Ba$_{MA}$, Zn$_{MA}$, and Cd$_{MA}$) as donors and on Pb site (Sr$_{Pb}$, Ba$_{Pb}$, Zn$_{Pb}$, and Cd$_{Pb}$) as neutral defects. We have considered group-IIIA elements, Al, Ga, and In, and group VA elements, Sb and Bi, on Pb sites (Al$_{Pb}$, Ga$_{Pb}$, In$_{Pb}$, Sb$_{Pb}$, and Bi$_{Pb}$) as potential donors. We have considered O, S, Se, and Te on Br sites (O$_{Br}$, S$_{Br}$, Se$_{Br}$, and Te$_{Br}$) as potential acceptors.
Figure 4-6: Calculated transition energy levels of shallow donors and shallow acceptors.

The calculated transition energy levels of identified shallow donors are shown in the left part of Figure 4-6. The transition energy levels are referenced to the CBM of CH$_3$NH$_3$PbBr$_3$. It shows that interstitial group IA and IB elements, Na$_i$, K$_i$, Rb$_i$, and Cu$_i$, are shallow donors. Group IIA elements such as Sr and Ba at MA sites are not very shallow donors. They are neutral defects when they occupy Pb sites. Our calculations revealed that Zn$_{MA}$, Cd$_{MA}$, Al$_{Pb}$, Ga$_{Pb}$, and In$_{Pb}$ are deep donors. Therefore, these dopants are not considered further in this paper. Bi$_{Pb}$ and Sb$_{Pb}$ are donors with transition energy levels of -0.189 eV and -0.231 eV, respectively.

The calculated transition energy levels of the identified shallow acceptors are shown in the right part of Figure 4-6. The transition energy levels are referenced to the VBM of CH$_3$NH$_3$PbI$_3$. The calculated transition energy levels of Na$_{Pb}$, K$_{Pb}$, Rb$_{Pb}$, and Cs$_{Pb}$ are -0.025 eV, -0.013 eV, -0.013 eV, and 0.003 eV, respectively. The calculated transition energy levels for O$_{Br}$, S$_{Br}$, Se$_{Br}$, and Te$_{Br}$ are -0.080 eV, 0.067 eV, 0.096 eV, and 0.148 eV, respectively. The negative transition energies indicate spontaneous ionizations.

While the calculated transition energy levels show that many of the considered dopants produce shallow donors and acceptors, the extrinsic doping properties of
CH$_3$NH$_3$PbBr$_3$ rely on the positions of Fermi levels determined by the formation of all defects including intrinsic and extrinsic defects. To evaluate the extrinsic doping properties of CH$_3$NH$_3$PbBr$_3$, we have calculated the formation energies of the above dopants with shallow transition energies under three representative growth conditions: A (Br-rich/Pb-poor), B (moderate), C (Br-poor/Pb-rich).

Surprisingly, we find that all the above dopants are not able to influence the conductivity of CH$_3$NH$_3$PbBr$_3$. In most cases, the electrical conductivities are determined by the intrinsic defects due to the much lower formation energies of some shallow intrinsic defects such as V$_{\text{Pb}}$ at Pb-poor/Br-rich conditions and V$_{\text{Br}}$ and V$_{\text{Pb}}$ at Pb-rich/Br-poor conditions. For example, Figures 4-7(a), 4-7(b), and 4-7(c) show the calculated formation energies as functions of Fermi levels for group IA and IB dopants at Br-rich/Pb-poor, moderate, and Br-poor/Pb-rich growth conditions, respectively. The dashed line shows the intrinsic defects with the lowest formation energies. It is seen that at Br-rich/Pb-poor condition (Fig. 4-7(a)), the formation energies of acceptors of Na$_{\text{Pb}}$, K$_{\text{Pb}}$, Rb$_{\text{Pb}}$, and Cu$_{\text{Pb}}$ are much lower than that of the donors, Na$_{\text{i}}$, K$_{\text{i}}$, Rb$_{\text{i}}$, and Cu$_{\text{i}}$. However, the formation energies for V$_{\text{Pb}}$ are even lower at all Fermi level positions. Therefore, for doping with group IA and IB elements at Br-rich/Pb-poor conditions, the electric conductivity is determined solely by the formation of V$_{\text{Pb}}$, which pins the Fermi level inside the VB. Therefore, the extrinsic dopants do not make any contribution to the p-type conductivity of CH$_3$NH$_3$PbBr$_3$ at Br-rich/Pb-poor growth conditions. At the moderate condition (Fig. 4-7(b)), only Na$_{\text{Pb}}$ pins the Fermi level at 0.19 eV above the VBM (indicated by marked by the left vertical dashed line), which is only 0.06 eV lower than the Fermi level of 0.25 eV (indicated by the right vertical dashed line) pinned by the
intrinsic defects of $V_{Br}$ and $V_{Pb}$. Therefore, Na doping may lead to a slightly improved p-type $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Doping using other group IA and IB elements would not improve the p-type conductivity. A similar situation is seen for the doping at the Br-poor/Pb-rich condition (Fig. 4-7(c)). Therefore, doping using group IA and IB elements is not expected to change significantly the conductivity of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. For doping using group-IIA (Fig. S1) and group-VIA (Fig. S2) elements, it is also found that the conductivities are determined solely by the intrinsic defects such as $V_{Pb}$ and $V_{Br}$. As discussed earlier, the antibonding coupling between Pb $s$ and Br $p$ orbitals is stronger than that between Pb $s$ and I $p$ orbitals. Therefore, the formation of $V_{Pb}$ and $V_{Br}$ is expected to be easier in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ than in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Therefore, the compensation from $V_{Pb}$ and $V_{Br}$ is more prominent in $\text{CH}_3\text{NH}_3\text{PbBr}_3$. This partially explains why extrinsic doping does not influence the electric properties of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. 
Figure 4-7: Calculated formation energies of defects formed by group-IA and -IB elements as functions of the Fermi levels at (a) Br-rich/Pb-poor, (b) moderate, and (c) I-poor/Pb-rich conditions. The intrinsic defects with the lowest formation energies are shown as the dashed line. The vertical dotted lines indicate the Fermi level pinning. The Fermi levels are referenced to the VBM.

It should be noted that the above calculations are only valuable for the situations under thermal equilibrium growth conditions. The calculated transition energy levels provide guidance for doping CH$_3$NH$_3$PbI$_3$ using non-thermal equilibrium approaches, such as post-deposition diffusion. For example, Sr$_{MA}$ and Ba$_{MA}$ are found to be shallow donors. These donors may be introduced by diffuse Sr$^{2+}$ or Ba$^{2+}$ ions into CH$_3$NH$_3$PbI$_3$ films grown under CH$_3$NH$_3$-poor conditions. Sr$^{2+}$ or Ba$^{2+}$ ions will fill in the V$_{MA}$ sites and turn CH$_3$NH$_3$PbI$_3$ films into n-type.

4.4 Conclusion
In summary, our calculations have shown that despite a large band gap of 2.2 eV, the dominant defects in CH$_3$NH$_3$PbBr$_3$ create only shallow levels, indicating a low bulk non-radiative recombination rate. These unusual defect properties explain partially why CH$_3$NH$_3$PbBr$_3$–based solar cells are able to achieve high V$_{OC}$’s. We have further shown that the photovoltaic properties of CH$_3$NH$_3$PbBr$_3$–based perovskite absorbers can be tuned via defect engineering. CH$_3$NH$_3$PbBr$_3$ with low carrier concentration, i.e., required for good solar cell absorbers, can be grown under moderate growth conditions. Under Br-rich/Pb-poor growth conditions, highly conductive p-type CH$_3$NH$_3$PbBr$_3$ films are expected, which may be used as low-cost hole transporting materials for lead halide perovskite solar cells. We have further suggested that n-type CH$_3$NH$_3$PbBr$_3$ should be produced through post-deposition diffusion of alkaline or alkaline earth metal ions.
Chapter 5

Structural, Electronic and Optical Properties of Cu$_3$-V-VI$_4$ Compounds: a First Principle Study

The structural, electronic and optical properties of Cu$_3$-V-VI$_4$ compounds are studied using first-principles density-functional theory with the HSE06 hybrid functional. Four different wurtzite-based and zinc-blende-derived crystal structures, enargite, wurtzite-PMCA, famatinitie and zinc-blend-PMCA, have been considered. We find that Cu$_3$PS$_4$ and Cu$_3$PSe$_4$ prefer energetically the enargite structure, whereas, other compounds favor the famatinitie structure. Among the compounds and structures considered, enargite Cu$_3$PSe$_4$, and famatinitie Cu$_3$AsS$_4$, are suitable for single junction solar cell applications due to bandgaps of 1.32 eV and 1.15 eV, respectively.

5.1 Introduction

Chalcogenide semiconductors have demonstrated their potentials for the applications in thin-film photovoltaic solar cells – polycrystalline CdTe-, CuInSe$_2$-, and Cu$_2$ZnSnSe$_4$-based thin-film solar cells have reached efficiencies of 19.6%, 21.7%, and 11.1%, respectively [64], surpassing their single crystal counterparts. CdTe, CuInSe$_2$, and Cu$_2$ZnSnSe$_4$ belong to the binary II-VI, ternary I-III-VI$_2$, and quaternary I$_2$-II-IV-VI$_2$,
respectively. Relative to binary CdTe chalcogenides, ternary I-III-VI$_2$ and quaternary I$_2$-II-IV-VI$_2$ compounds can be obtained by mutating the group II atoms and maintaining the electron octet rule [81-83]. The ternary and quaternary chalcogenide semiconductors exhibit more flexible properties due to their enhanced structural and chemical choice. Therefore, the electronic and structural properties of ternary I-III-VI$_2$ and quaternary I$_2$-II-IV-VI$_2$ compounds have been studied extensively [84-92]. Structurally, all these chalcogenide compounds consist of high symmetry ACh$_4$ tetrahedron units, where A is one of the cation elements and Ch is one of the chalcogenide elements. It has been considered that these high symmetry structural units are critical for these compounds to exhibit excellent electronic properties that are necessary for achieving high efficiency solar cells.

Beside I-III-VI$_2$, there exist another ternary chalcogenide compounds that also obey the electron octet rule and consist of ACh$_4$ tetrahedron units: I$_3$-V-VI$_4$. The group-I elements are Cu and Ag, and the group-V elements include P, As, Sb, and Bi. The I$_3$-V-VI$_4$ ternary compound semiconductors may also have the potential for electronic device applications. For example, Cu$_3$PS$_4$ and Cu$_3$PSe$_4$ have shown photoelectrochemical response [93]. Cu$_3$SbSe$_4$ has been considered a candidate for thermoelectric applications [94,95]. Recent reflectance spectroscopy measurements have shown that Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ have a bandgap of 1.4 eV, which is ideal for the applications of photovoltaic solar cells [96]. Nonetheless, the I$_3$-V-VI$_4$ chalcogenide semiconductors have received much less attention as compared with I-III-VI$_2$, and I$_2$-II-IV-VI$_2$ chalcogenide semiconductors.

5.2 Method Details
Our first-principles calculations are based on DFT using projector augmented wave method and the generalized gradient approximation (GGA-PBE) [23, 57] as implemented in the Vienna ab-initio simulation package (VASP) [28]. For the calculation of electronic and optical properties, we used the Heyd-Scuseria-Ernzerhof (HSE) [97] hybrid functional. 25% of the GGA exchange potential is replaced by exact Hartree-Fock exchange potential to avoid the bandgap underestimation. A well-converged plane-wave basis set with a cutoff energy of 400 eV was used. For total energy calculations, we used orthorhombic supercells with 32 atoms for wurtzite-derived system and tetragonal supercell with 16 atoms for zinc-blend derived system. Monkhorst-Pack k-point sampling \((6\times3\times7)\) and \((7\times7\times3)\) were used for orthorhombic and tetragonal cells respectively. All atoms were fully relaxed until the forces become smaller than 0.01 eV/Å.

5.3 Results and Discussion

We systematically study the structural, electronic and optical properties of Cu\textsubscript{3}-V-VI\textsubscript{4} compounds using first-principles density-functional theory (DFT) with the HSE06 hybrid functional. The group-V elements include P, As, Sb, and Bi and the group-VI elements include S, Se, and Te. Four different wurtzite-based and zinc-blende-derived crystal structures, enargite, wurtzite-primitive-mixed CuAu (PMCA), famatinite and zinc-blend-PMCA, are considered. These structures maintain the high symmetry ACh\textsubscript{4} tetrahedron units and obey the electron octet rule. We find that Cu\textsubscript{3}PS\textsubscript{4} and Cu\textsubscript{3}PSe\textsubscript{4} prefer energetically the enargite structure, whereas other compounds favor the famatinite structure. Among the compounds and structures considered, enargite Cu\textsubscript{3}PSe\textsubscript{4}, and
famatinite Cu₃AsS₄, are suitable for single junction photovoltaic solar cell applications due to their bandgaps of 1.32 eV and 1.15 eV, respectively. The enargite Cu₃PS₄ and famatinite Cu₃AsSe₄ have bandgaps of 2.51 eV and 2.42 eV, respectively. Cu₃SbS₄ and Cu₃PSe₄ can exist in some structures and exhibit bandgaps from 0.78 eV to 0.88 eV. These materials can be used as the absorbers in the top and bottom cells in the three-junction tandem cells.

Firstly we study the energetic stability of the Cu₃-V-VI₄ (V = P, As, Sb, Bi and VI = S, Se, Te) chalcogenide compounds. The crystal structures of the stable Cu₃-V-VI₄ (V = P, As, Sb, Bi and VI = S, Se, Te) chalcogenide compounds should meet the electron octet rule, which requires that every anion atom has a total of 8 out shell valence electrons. For Cu₃-V-VI₄, each anion must be bonded to three group-I atoms and one group-V atom. To satisfy the octet rule, Cu₃-V-VI₄ can have four different crystal structures: enargite (space group Pmn2₁), wurtzite-PMCA (space group P6₃mc), famatinite (space group I4₂m), and zinc-blend-PMCA (space group P4₃m). The enargite and wurtzite-PMCA structures are based on the wurtzite configuration, while the famatinite and zinc-blend-PMCA structures are based on the zinc-blende configuration. Figure 5-1 depicts the details of the four crystal structures. The enargite structure and the famatinite structure have the same cation ordering. The (0001) planes of the enargite structure are the same as the (111) planes of the famatinite structure. The wurtzite-PMCA structure and the zinc-blend-PMCA structure have the same relation: the (0001) planes of the wurtzite-PMCA structure are the same as the (111) planes of the zinc-blend-PMCA structure. The arrows in Fig. 5-1 show these relations.
Figure 5-1: Four different crystal structures: (a) Enargite; (b) Famatinite; (c) Wurtzite-PMCA; (d) Zinc-blende-PMCA
Table 5.1. The calculated relative total energies (meV/atom) and the corresponding band gap values of ternary semiconductors Cu₃-V-VI₄ (V=P, As, Sb, Bi; VI=S, Se, Te) in four crystal phases. The energies are referred to that of the enargite structure. The energy value of the most stable phase is **bolded** for each compound. Considering the superscript in the column of band gap value, *i* and *d* indicate indirect and direct bandgaps respectively.

<table>
<thead>
<tr>
<th>Structure</th>
<th>(a) Enargite</th>
<th>(b) Faminatite</th>
<th>(c) Wurtzite</th>
<th>(d) Zinc-blende</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>E</em>ₜₜₜ</td>
<td><em>E</em>ₜₜₜ</td>
<td><em>E</em>ₜₜₜ</td>
<td><em>E</em>ₜₜₜ</td>
</tr>
<tr>
<td>Cu₃PS₄</td>
<td>0</td>
<td>2.5¹</td>
<td>6.03</td>
<td>2.4²</td>
</tr>
<tr>
<td>Cu₃AsS₄</td>
<td>0</td>
<td>1.3⁴</td>
<td>-4.31</td>
<td>1.1⁵</td>
</tr>
<tr>
<td>Cu₃SbS₄</td>
<td>0</td>
<td>0.8⁶</td>
<td>-9.91</td>
<td>0.8⁸</td>
</tr>
<tr>
<td>Cu₃BiS₄</td>
<td>0</td>
<td>--</td>
<td>-5.25</td>
<td>--</td>
</tr>
<tr>
<td>Cu₃PSe₄</td>
<td>0</td>
<td>1.3²</td>
<td>2.03</td>
<td>1.3¹</td>
</tr>
<tr>
<td>Cu₃AsSe₄</td>
<td>0</td>
<td>0.3⁷</td>
<td>-11.28</td>
<td>0.2²</td>
</tr>
<tr>
<td>Cu₃SbSe₄</td>
<td>0</td>
<td>--</td>
<td>-13.94</td>
<td>--</td>
</tr>
<tr>
<td>Cu₃BiSe₄</td>
<td>0</td>
<td>--</td>
<td>-8.47</td>
<td>--</td>
</tr>
<tr>
<td>Cu₃PTe₄</td>
<td>0</td>
<td>0.3⁹</td>
<td>-5.47</td>
<td>0.3²</td>
</tr>
<tr>
<td>Cu₃AsTe₄</td>
<td>0</td>
<td>--</td>
<td>-11.25</td>
<td>--</td>
</tr>
<tr>
<td>Cu₃SbTe₄</td>
<td>0</td>
<td>--</td>
<td>-11.38</td>
<td>--</td>
</tr>
<tr>
<td>Cu₃BiTe₄</td>
<td>0</td>
<td>--</td>
<td>-7.19</td>
<td>--</td>
</tr>
</tbody>
</table>
The calculated total energies per atom for the Cu$_3$-V-VI$_4$ compounds with four crystal structures are listed in Table 5.1. It is seen that the enargite structure is the ground state only for Cu$_3$PS$_4$ and Cu$_3$PSe$_4$. All other compounds have the Famatinite structure as their ground state. None of the compounds has the wurtzite-PMCA structure or the zinc-blende-PMCA structure as its ground states, but the energy difference among them is small. The results are consistent with available experimental data. For example, it has been reported that Cu$_3$PS$_4$ and Cu$_3$PSe$_4$ possess the enargite structure with the space group of \( \text{Pmn2}_1 \) [98-99]. Reports have also indicated that Cu$_3$AsS$_4$, Cu$_3$SbS$_4$, Cu$_3$SbSe$_4$ should have the famatinite structure with the space group of \( \text{I}4_2m \) [100-102]. A report has also considered enargite structure for Cu$_3$AsS$_4$, but our calculation shows the famatinite structure is more stable by 4.31 meV/atom. Usually, crystal structures with energy difference less than 10 meV (per atom) could coexist in experiment. Also, it should be pointed out that the calculations are the results for 0 K temperatures. Entropy may affect the structures when the materials are synthesized at elevate temperatures.

We calculated the band structures of Cu$_3$-V-VI$_4$ compounds to determine their bandgaps. For comparisons, the bandgaps of enargite, famatinite, wurtzite-PMCA and zinc-blende-PMCA structures were calculated. Hybrid HSE06 functional was used for obtaining accurate values of bandgaps. All calculated HSE bandgap values are listed in Table 5.1. We find that enargite Cu$_3$PSe$_4$, Cu$_3$AsS$_4$, Cu$_3$AsSe$_4$, Cu$_3$SbS$_4$, and famatinite Cu$_3$PSe$_4$, Cu$_3$SbS$_4$, wurtzite-PMCA Cu$_3$PSe$_4$, Cu$_3$AsS$_4$, Cu$_3$AsSe$_4$ and Cu$_3$SbS$_4$ have direct bandgaps, whereas enargite Cu$_3$PS$_4$ and Cu$_3$PTe$_4$, famatinite Cu$_3$PS$_4$, Cu$_3$AsS$_4$, Cu$_3$AsSe$_4$, and Cu$_3$PTe$_4$, wurtzite-PMCA Cu$_3$PS$_4$ and zinc-blende PMCA Cu$_3$PS$_4$, Cu$_3$AsS$_4$, and Cu$_3$SbS$_4$ have indirect bandgaps. The rest have zero or negative bandgaps.
In addition, the calculated bandgaps show a clear trend: the bandgap decreases as the atomic number of the V or VI element increases. For example, for the enargite structure, the bandgap is 2.51 eV for Cu$_3$PS$_4$. It decreases to 1.34 eV for Cu$_3$AsS$_4$, and then to 0.86 eV for Cu$_3$SbS$_4$, and finally to the metal state (< 0 eV) for Cu$_3$BiS$_4$. For the same structure, the bandgaps of Cu$_3$PS$_4$, Cu$_3$PSe$_4$, and Cu$_3$PTe$_4$ are 2.51 eV, 1.32 eV, and 0.39 eV, respectively. Therefore, the Cu$_3$-V-VI$_4$ ternary compounds exhibit a large range of bandgaps, which can be used for various applications, shown in Fig. 5-2. For photovoltaic applications, the optimal bandgaps are in the range of 1.1 – 1.6 eV. For example, Cu$_3$PSe$_4$, which has a bandgap of 1.32 eV in the structure of enargite and 1.31 eV in the structure of famatinite, and Cu$_3$AsS$_4$, which has a bandgap of 1.34 eV in the structure of enargite and 1.15 eV in the structure of famatinite, have the potential for applications in single-junction based solar cells. For multijunction solar cells, materials with bandgaps both larger and smaller than 1.1-1.6 eV are needed. Cu$_3$PS$_4$, which has a bandgap of 2.51 eV in the structure of enargite and 2.42 eV in the structure of famatinite, may be used as the top cells. Cu$_3$SbS$_4$, Cu$_3$AsSe$_4$, and Cu$_3$PTe$_4$, which have bandgaps in the range of 0.4 eV – 0.9 eV, may be used as the bottom cells. Enargite Cu$_3$PSe$_4$ has been synthesized experimentally and the measured bandgap is about 1.4 eV [97]. Our calculated bandgap for enargite Cu$_3$PSe$_4$ is 1.32 eV, in good agreement with the experimental bandgap value.
Figure 5-2: Bandgaps of Cu-V-VI$_4$ compounds in different crystal phases and their potential applications in single junction, top and bottom solar cell absorbers.

To understand the bandgap trend for Cu$_3$-V-VI$_4$ ternary compounds, we have calculated the total and partial densities of states (DOS) of the compounds for both the enargite and the famatinite structures. Detailed analysis of the partial and total DOS reveal that the upper valence bands of these compounds are derived from Cu $d$ and VI $p$ states, whereas the lower conduction bands are derived from mainly the V $s$ states with a small component of VI $p$ states. As an example, the total and partial DOS of enargite Cu$_3$PSe$_4$ are shown in Fig. 5-3. The formation of the upper valence bands and lower
conduction bands imply that the observed bandgap trend can be explained by the energy trend of the out shell $p$ orbitals of the group-VI elements and the out shell $s$ orbitals of group-V elements. From P to As, to Sb, and to Bi, the out shell $s$ orbital decreases in energy. Also, the larger atomic size leads to smaller band gap. Therefore, if the VI element remains the same, the conduction band minima (CBM) of the Cu$_3$-V-VI$_4$ compounds will decrease in energy as the V element changes from P to Sb, and to Bi, leading to decrease on bandgap. For group-VI elements, the out shell $p$ orbital increases in energy from S to Se and to Te. If the V element remains the same, the valence band maxima (VBM) of the Cu$_3$-V-VI$_4$ compounds will increase in energy from S to Se and to Te, leading to reduction on bandgaps.
Figure 5-3: The total and partial density of states of the ground states of enargite Cu$_3$PSe$_4$.

The calculated bandgaps of enargite Cu$_3$PSe$_4$ and famatinite Cu$_3$AsS$_4$ indicate that these compound semiconductors are suitable for the applications in single-junction solar cells. Good candidates for photovoltaic applications must also have good optical
absorption. We have therefore calculated the optical absorption properties of enargite Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ using HSE06 functional. The imaginary part of the calculated dielectric functions of Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ are shown in Fig. 5-4, where all the diagonal elements are averaged. The overall shapes of these two compounds are similar, due to their similar band component near the gap. The energy threshold from zero to nonzero dielectric function is similar too because of their close band gap values. So these properties indicate their absorption of light is also comparable, but a little different in the onset-to-absorption frequency, here like the light absorption around 4 eV.

**Figure 5-4:** The calculated imaginary dielectric functions of enargite Cu$_3$PSe$_4$ and enargite Cu$_3$AsS$_4$ using HSE06 functional.
5.4 Conclusion

In summary, we have systematically studied the structural, electronic, and optical properties of Cu$_3$-V-VI$_4$ compounds using first-principles DFT with the HSE06 hybrid functional. We found that Cu$_3$PS$_4$ and Cu$_3$PSe$_4$ prefer energetically the enargite structure, whereas other compounds favor the famatinite structure. Considering the small energy differences (< 5 meV/atom) among the compounds with different structures, a large variety of phases may exist. The enargite Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ have bandgaps of 1.32 and 1.34 eV, respectively. Famatinite Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ have bandgaps of 1.31 and 1.15 eV, respectively. These materials are suitable for the applications in single junction photovoltaic solar cell. Cu$_3$PS$_4$ has a bandgap of 2.51 eV in the structure of enargite and 2.42 eV in the structure of famatinite. Cu$_3$SbS$_4$, Cu$_3$AsSe$_4$, and Cu$_3$PTe$_4$ have bandgaps in the range of 0.4 eV – 0.9 eV. These materials can be used as the absorbers for the top and bottom cells in the three-junction tandem cells.
Chapter 6

Intrinsic Physics Properties in Copper Antimony Sulfide Compounds

Intrinsic physics properties in earth abundant copper antimony sulfide compounds, CuSbS2 and Cu3SbS4 are studied by density functional theory and HSE06 hybrid functional. The chalcostibite CuSbS2 has an indirect band gap of 1.85 eV, whereas the chalcogenide Cu3SbS4 has a direct band gap of 0.89 eV. We find that the large difference on band gaps is mainly attributed to the different Sb charge states. We further find that the Sb charge states also affect the defect physics. Particularly, the Sb lone pair s orbitals in CuSbS2 have strong influence on the formation energy of Sb-related defects.

6.1 Introduction

Shockley queissner limitation of photovoltaic materials describes the proper band gap value is the critical factor for solar cell to reach the high spectroscopic limited maximum efficiency [49]. The bigger band gap values the materials have, the higher open circuit voltage for increasing the efficiency they will get. However, according to the real solar spectrum, the balance between open circuit voltage and the short circuit current
must be considered. The S-Q limit tells us one of the best semiconductor choices is
GaAs with 1.52eV. So promising new absorber materials should have the proper band
gap value and strong absorption across the solar spectrum. Direct band gap value around
1.0 eV is good for allowing the direct optical transition of visible lights. In this work, we
compare two potential absorber materials CuSbS$_2$ and Cu$_3$SbS$_4$ and describe their
potential for the possible application. Moreover, in our calculation the efficiencies of
these two compounds are higher than the one of GaAs when the thin film is less than one
micrometer, due to their distinguishing absorption properties. The band localization near
the conduction band maxima will increase the density of states for transitions, and finally
will enhance the absorption. So the efficiency of CuSbS$_2$ and Cu$_3$SbS$_4$ will go higher than
the efficiency of GaAs.

Currently, the technologies of thin film solar cell are mainly based on the visible
light absorbing materials: CdTe and CuIn$_{1-x}$Ga$_x$Se$_2$. However, as the development of
photovoltaic goes fast, only the lower-cost, non-toxic, earth abundant absorber materials
with good efficiency will satisfy the pressing need for the sustainable, scalable and
commercial application of PV. After expanding the searching range of different absorber
materials, quaternary CZTS materials begin to thrive from 2009 and the ternary CuSbS
thin film absorber materials also gather much interest. Considering the scarcity of In,
Ga, Te and toxic Cd, CZTS and CuSbS should have the long-term developed potential.
The multivariant compounds also exhibit more flexible properties values because of their
enhanced structural and chemical choices. The ternary and quaternary compounds can
have the wide band gap range by tuning the compositions of their elements. Meanwhile,
more possibilities on design will give the higher risk of the complication. Compared with
the quaternary CZTS, ternary CuSbS should be less complicated on phases and doping problem. Previously, ternary chalcogenide Cu\textsubscript{3}-IV-VI\textsubscript{4} and chalcostibite CuIV-VI\textsubscript{2} has been separately studied from different perspectives in many researches [96, 103-109]. The chalcogenide structures are often granted as one of the best candidates for achieving the high efficiency because their high symmetry ACh\textsubscript{4} tetrahedron units are critical for the compounds to exhibit excellent electronic properties, where A is one of the cation elements and Ch is one of the chalcogenide elements. In our work, we find the lone pair s-state of Sb will play an unusual role to a different crystal structure_chalcostibite system.

We compare two compounds: chalcogenide Cu\textsubscript{3}SbS\textsubscript{4} and chalcostibite CuSbS\textsubscript{2} in detail, not only from the optical and electronic properties, also depicting their possible doping situation and the potential for the applications.

### 6.2 Method Details

Our first-principles calculations are based on DFT using projector augmented wave method[30] and the generalized gradient approximation (GGA-PBE) [23, 57] as implemented in the Vienna ab-initio simulation package (VASP) [28-31]. For the calculation of electronic and optical properties, we used the Heyd-Scuseria-Ernzerhof (HSE) [97] hybrid functional. 25% of the GGA exchange potential is replaced by exact Hartree-Fock exchange potential to avoid the bandgap underestimation. A well-converged plane-wave basis set with a cutoff energy of 400 eV was used. For total energy calculations, we used orthorhombic supercells with 32 atoms for wurtzite-derived system and tetragonal supercell with 16 atoms for zinc-blend derived system. Monkhorst-Pack k-point sampling (6×3×7) and (7×7×3) were used for orthorhombic and tetragonal cells.
respectively. All atoms were fully relaxed until the forces become smaller than 0.01 eV/
Å.

6.3 Results and Discussion

6.3.1 Crystal Structures

Sidgwick and Powell pointed out the simple electrostatic theory for the arrangement in space of the covalencies of multicovalent atoms in 1940. It stated that the pairs of electrons in a valence shell are always arranged in the same way which depends only on their number. Based on this theory, Gillespie further described the regular shapes of atoms when all the electron pairs are forming bonds with the same kind of atom or group and the deviation of the regular structures if the lone pair existed [108]. So the hybrid sp\(^3\) orbitals will give the tetrahedral atomic shape if no lone pair exist, while form the pyramidal shape if there is one lone pair orbitals. The chalcogenide compound Cu\(_3\)SbS\(_4\) consist of high symmetry SbS\(_4\) tetrahedron units which is critical for its good electronic properties. The excellent reproduction of the observed crystal structures of chalcostibite CuSbS\(_2\) is based on the unusual SbS\(_5\) coordination geometry. The classical valence shell electron pair repulsion (VSEPR) theory stated the lone pair s electrons occupy a non-bonding orbits, but directly control its atomic coordination and its structural packing electrostatically [109].

The crystal structures of the stable ternary Cu-Sb-S compounds, no matter it is chalcogenide or chalcostibite structure, should meet the electron octet rule, which requires that every canion atom has full shell valence electrons, shown in the pink and
green shadow units of figure 6-1. The chalcogenide compounds $\text{Cu}_3\text{SbS}_4$ obey the electron octet rule and consist of $\text{SbS}_4$ tetrahedron units, while the chalcostibite are composed of the edge-sharing pyramidal $\text{SbS}_5$ units and $\text{SbS}_2$ units. For $\text{Cu}_3\text{SbS}_4$, each S atom must be bonded to three Cu atoms and one Sb atom. Actually, there are four different crystal structures of $\text{Cu}_3\text{SbS}_4$ satisfying the octet rule: enargite (space group $Pmn2_1$), wurtzite-PMCA (space group $P6_3mc$), famatinite (space group $I4\bar{2}m$), and zinc-blend-PMCA (space group $P\bar{4}3m$). Here we only choose its most stable famatinite structure which is based on the zinc-blende configuration. The chalcostibite structure also need to obey the octet rule, but follow a special structural characteristic. The tetrahedral $\text{CuS}_4$ unit of orthorhombic $\text{CuSbS}_2$ (space group $Pnma$) will separate its other two continuous units $\text{SbS}_2$ and $\text{SbS}_5$ and force their Sb atoms direct the opposite way, indicated by the insert figure 6-1. Thus the lone pair s electron density of Sb will go into the void between two $\text{SbS}_3$ units and affect the dispersion of its valence band maximum.
6.3.2 Electronic Properties

We have calculated the total and partial densities of states (DOS) of the compounds for both chalcostibite and chalcogenide structures, shown in figure 6-2. For the chalcostibite CuSbS$_2$, the partial and total DOS reveal that upper valence bands are derived from Cu-$d$ and S-$p$ states, also with some Sb-$s$ and Sb-$p$, whereas the lower conduction bands are derived from mainly the Sb-$p$ state. For the chalcogenide Cu$_3$SbS$_4$, its upper valence band is derived from Cu-$d$ and S-$p$ states, whereas the lower conduction bands are derived from mainly the Sb-$s$ states with a small component of S-$p$ states. The different valence states of Sb will play a critical role on the difference of electronic
properties of Cu-Sb-S compounds. Sb is +5 in Cu$_3$SbS$_4$; while Sb is +3 in CuSbS$_2$. So the outshell electrons from s and p orbits will contribute differently for composing the valence band maximum and conduction band minimum. In our calculation, we can tell the obvious difference of these two compounds, indicated by the red arrow. The Sb lone pair s will help the chalcostibite CuSbS$_2$ compound form the conduction band. But in chalcogenide Cu$_3$SbS$_4$ system, Sb atom will lose its whole five valence electrons and thus the corresponding s and p orbitals will form the valence band.

![Density of states of chalcostibite CuSbS$_2$ and chalcogenide Cu$_3$SbS$_4$](image)

**Figure 6-2:** Density of states of chalcostibite CuSbS$_2$ and chalcogenide Cu$_3$SbS$_4$

To understand the electronic properties further of these two different compounds, we also calculated their band structures. As shown in Fig. 6-3, the chalcostibite CuSbS$_2$
has the bigger indirect band gap, and its band gap value is 1.85 eV in our HSE-GGA calculation, which is slightly overestimated in contrast to the experimental value 1.52 eV; the chalcogenide Cu$_3$SbS$_4$ has the smaller direct band gap, and its band gap value is 0.89 eV in our HSE-GGA calculation, which is consistent with the experimental value 0.88 eV very well. The band gaps will be severely underestimated using a standard GGA functional because of the under-estimation of the d orbital interaction. Moreover, the lone-pair interactions will be under-estimated too in the chalcostibite system. So the chalcostibite structure is more sensitive to the K-grids in our HSE calculations. It also explains why the HSE indirect band gap value of CuSbS$_2$ is slightly over-estimated. Another obvious difference between CuSbS$_2$ and Cu$_3$SbS$_4$ based on the observation of band structures is the density state around the conduction band edges. Since the Sb-$s$ band is characterized by a rather wide dispersion and brings a broad density of state, the density state near the CBM of chalcogenide Cu$_3$SbS$_4$ is lower than the one of chalcostibite CuSbS$_2$. So the photon energy absorption of these two compounds will act differently based on their distinguishing electronic properties. Although CuSbS$_2$ has the indirect band gap, but the difference between the lowest energy direct and indirect gaps is only of the order of 0.1 eV, so a strong onset of optical absorption is still expected.
6.3.3 Optical Properties and Maximum Efficiency

There are two important trends in figure 6-4. Firstly, it indicates that the absorption of ternary compounds Cu-Sb-S surpass the absorption of binary GaAs when the film thickness is less than 1μm. As the thickness is increasing, we found the final maximum efficiency of GaAs will become the largest, compared with the other two ternary compounds. Also, the final efficiency of chalcogenide Cu₃SbS₄ is bigger than the one of chalcostibite CuSbS₂. Considering the transition channels of absorption, the ternary of Cu-Sb-S first benefit from the steeper absorption because of the higher density of states near CBM, compared with the binary semiconductor GaAs. In binary material,
the absorption at threshold occurs from the anion p-like VBM to the cation s-like CBM. While in the ternary chalcostibite systems, the absorption transition happened from the Cu-d plus S-p of VBM to Sb-p near CBM; in the ternary chalcogenide systems, the absorption transition happened from the Cu-d plus S-p of VBM to Sb-s plus S-s near CBM. The higher Cu/Sb ratio in $\text{Cu}_3\text{SbS}_4$ and the more dispersive p-orbit VBM caused by lone pair orbit in $\text{CuSbS}_2$ both contribute the localization of density of states, and thus enhance the absorption. However, the final maximum efficiency just depends on the band gap values.
Figure 6-4: Imaginary dielectric functional of chalcostibite CuSbS$_2$ and chalcogenide Cu$_3$SbS$_4$ and their corresponding maximum efficiencies
6.4 Conclusion

Chalcogenide Cu$_3$SbS$_4$ and chalcostibite CuSbS$_2$ are the better candidates as the new potential PV absorber materials. Normally, the chalcogenide structure with high symmetric ACh4 unit should behave the good properties for the PV application. Interestingly, the lone pair dispersive s state of Sb atom will play an unusual role in the chalcostibite structure. The higher Cu/V ratio in chalcogenide structure will localize the bands near CBM and lead to an increase in the DOS for transition, finally enhance the corresponding absorption. For the chalcostibite structure, the lone pair s will bring the void separation between SbS$_5$ units and form the bond-edge sharing structure externally. So the intrinsic electronic properties will behave distinguish corresponding to the structural characteristics: CBM become less dispersive and offer the high density of states for the good absorption. In addition, the intrinsic doping situations are totally different between the CuSbS$_2$ system and the Cu$_3$SbS$_4$ system due to their structural distortions after doping.
Chapter 7

First-principles Study of Aluminum and Oxygen Defect Complexes in Silicon

The atomic structure and electronic properties of aluminum (Al)-related defect complexes in silicon are investigated using first-principles calculations. Individual substitutional Al (Al$_{\text{Si}}$), interstitial Al (Al$_{\text{i}}$) and their possible complex configurations with oxygen (O) atoms are studied. We find a unique stable complex configuration consisting of an Al$_{\text{i}}$ and an oxygen dimer, Al$_{\text{i}}$-2O$_{\text{i}}$, which introduces deep levels in the band gap of Si. The formation energies of the Al$_{\text{i}}$-2O$_{\text{i}}$ complexes could be lower than that of individual Al$_{\text{i}}$ atoms under oxygen-rich conditions. The formation of Al$_{\text{i}}$-2O$_{\text{i}}$ complexes may explain the experimental observation that the coexistence of Al and O results in reduced carrier lifetime in Si wafers.

7.1 Introduction

Silicon (Si) is one of the most abundant elements in the earth’s crust. It is a semiconductor material suitable for photovoltaic applications. Multicrystalline and monocrystalline Si solar cells dominate the current photovoltaic market. More than 80% of the global solar-cell production is from Si-based cells [110, 111]. The photovoltaic
industry has been growing at a steady annual rate of 25-30% over the past several years and this progress is driven mainly by Si-based solar cells.

Aluminum (Al) is a common dopant for producing \( p \)-type Si. A substitutional Al (Al\(_{Si}\)) atom is a shallow acceptor. Thus, Al is often used as back contact to create back surface fields for Si-based solar cells. However, experimental results have shown that when Al and oxygen (O) coexist, the lifetime of the minority carriers in Si decreases dramatically [112-116]. It is speculated that Al and O may form complexes, causing the observed reduction of lifetime of minority carriers. However, the atomistic origin of the reduction mechanism is still unclear. Therefore, it is important to understand the structure and electronic properties of Al-O complexes.

Both Al and boron (B) belong to the group IIIA family. It is expected that Al and B may exhibit similar electronic properties in Si. B is also a dopant commonly used for producing \( p \)-type Si. B-O complexes have been found to be responsible for the experimentally observed reduction of carrier lifetime [117, 118]. Several theoretical models have been proposed to explain the effects of B-O complexes. It was predicted that interstitial B (B\(_i\)) trap an O dimer to form a bistable complex that produce a donor level in the upper half of the band gap of Si [119, 121]. Two distinctive configurations of B\(_i\)-2O\(_i\) complexes were reported in the literature: one is the \{B\(_i\), 2O\(_i\)\}-complex with a monoclinic-I symmetry and three-fold coordinated O atoms [119]; the other is that the O\(_i\) is bound to Si at a second nearest site to B [120]. The calculated electronic properties of the above two configurations of defect complexes using density-functional theory (DFT) are in good agreement with experimental observation: B-O complexes do not present detrimental effects to the minority carrier lifetime in Si. However, our DFT calculations
reveal a very different scenario for Al-O complexes in Si, even though B and Al belong
to the same group: an Al$_i$-2O$_i$ complex is identified to create deep gap states and therefore
are detrimental to the minority carrier lifetime in Si. In this paper, we study the energies,
configurations and electronic properties of Al-O defect complexes, and compare the
results with that of B-O defect complexes.

### 7.2 Method Details

Our first-principles calculations are based on DFT using all-electron projector
augmented wave method and the generalized gradient approximation (GGA-PBE) [23, 57], as implemented in the Vienna ab-initio simulation package (VASP) [28-31]. A well-
converged plane-wave basis set with a cutoff energy of 400eV was used. We used a
(10.95 Å ×10.95Å ×10.95 Å) cubic supercell with 64 atoms to model the studied defects.
A 3×3×3 grid was used for Monkhorst-Pack k-point sampling. All atoms were fully
relaxed until the forces become smaller than 0.01eV/ Å.

The ionization and formation energies of Al-O complexes were calculated by [62, 63]

$$
\varepsilon_g^F (\text{host}) - \varepsilon (0/q) = \left[ \varepsilon_{CBM}^F (\text{host}) - \varepsilon_b^F (0) \right] + \left[ E(\alpha, q) - \left( E(\alpha, 0) - q \varepsilon_b^F (0) \right) \right] / q \\
$$

$$
\Delta H_f (\alpha, q) = E(\alpha, q) + \sum n_i \mu_i + q E_F
$$

Here $\varepsilon_g^F (\text{host}) - \varepsilon (0/q)$ is the ionization energy, $\Delta H_f$ is the defect formation energy,
$E(\alpha, q)$ is the total energy for a supercell containing defect $\alpha$ in a charge state of $q$. The
formation energy also depends on the atomic chemical potentials $\mu_i$ and the electron
Fermi energy $E_F$. In this paper, we will only discuss the formation energies of Al-O
complexes in the charge neutral state.
7.3 Results and Discussion

It is known that individual Al atoms prefer energetically substitutional sites and act as shallow acceptors in Si. Individual O atoms prefer energetically at the bond center interstitial sites, acting as neutral dopants without strong influence on the electronic properties of Si [Fig. 7-1(a)]. However, when the concentration of O is high, multiple O atoms can aggregate together or combine with other impurities, such as B and Al atom, and result in different electronic properties than individual O atoms. In our work, all structures considered for B-O complex\textsuperscript{11} are considered for Al-O complexes. Furthermore, we examine several more configurations for Al-O complexes as described in Fig. 7-1.

Table. 7.1. Calculated total energies of supercells containing various Al-O complexes.

<table>
<thead>
<tr>
<th>Complexes of Al-O in Si</th>
<th>Total Energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{a-Al\textsubscript{Si}, 2O\textsubscript{i}}</td>
<td>-360.562</td>
</tr>
<tr>
<td>{b-Al\textsubscript{Si}, 2O\textsubscript{i}}</td>
<td>-358.989</td>
</tr>
<tr>
<td>{a-Al\textsubscript{i}, 2O\textsubscript{i}}</td>
<td>-363.701</td>
</tr>
<tr>
<td>{b-Al\textsubscript{i}, 2O\textsubscript{i}}</td>
<td>-362.136</td>
</tr>
<tr>
<td>{c-Al\textsubscript{i}, 2O\textsubscript{i}}</td>
<td>-362.968</td>
</tr>
</tbody>
</table>
Figure 7-1: Defect structures of Al-O complexes in Si considered in this paper.

7.3.1 O Thermal Donors
An isolated O atom prefers occupying a bond center interstitial site that has the similar configuration in silicon dioxide, and has not much influence on the electronic property of bulk Si [122, 123]. However, at high O concentration, several O atoms will aggregate together and form the thermal donor[124-127]. The configurations of O thermal donors are critical for studying B- or Al-related O defect complexes in Si. An individual O atom and a thermal donor consisting of 4 O atoms are shown in Fig. 1 (a) and (b), respectively. The key feature of the configuration of this thermal donor is the rhombohedra ring formed by two O and two Si atoms and the breaking of one Si-Si bond. The Si-Si bond breaking causes large atomic distortions around the defect core region. Without considering other impurities, the O rhombohedra ring must have at least four O atoms to become stable. To show the effects of individual O\textsuperscript{i} atoms and thermal donors, the calculated band structures for supercells without O atom, with one O\textsuperscript{i} and one thermal donor of four O atoms are shown in Figs. 2(a), 2(b), and 2(c), respectively. In Fig. 2(a) and 2(b), the highest occupied band is at the top of the valance band of the supercell as indicted by the lower dotted line. The O\textsuperscript{i} does not introduce any states in the band gap. In Fig. 2(c), the level indicated by the arrow is slightly below the conduction band minimum (CBM) of Si. The highest occupied state is indicated by $E_F$. Therefore, the thermal donor composed by four O\textsuperscript{i} atoms is a shallow donor and can be ionized by thermal energy at elevated temperature. However, if acceptor dopants such as B or Al present, the O thermal donor can be stable with only two O atoms.

**7.3.2 Al\textsubscript{Si} and O\textsuperscript{i} Complexes in Si**
Due to the strong ionic Al-O bonding, an Al\(_{\text{Si}}\) atom and an O\(_{\text{i}}\) atom favor to combine together, forming an Al\(_{\text{Si}}\)-O\(_{\text{i}}\) complex, which acts still as a shallow acceptor. Under O-rich condition, a Al\(_{\text{Si}}\) atom can combine with multiple O\(_{\text{i}}\) atoms. Such kind of defect complex was previously studied for B-O complexes by Sanati and Estreicher [120]. For (B, 2O\(_{\text{i}}\)), it was reported that the configuration shown in Fig. 6-1(d) [note: the configuration of B\(_{\text{Si}}\)-O\(_{\text{i}}\) complexes are adopted for Al\(_{\text{Si}}\)-O\(_{\text{i}}\) complex in our paper] is a more stable structure than the one shown in Fig. 7-1(c). Our results for the stability of the (B, 2O\(_{\text{i}}\)) configurations are consistent with that reported by Sanati and Estreicher\(^{11}\): the total energy of configuration shown in Fig. 7-1(d) is 0.23 eV lower than that of the configuration shown in Fig. 7-1(c). However, we find that the trend is different for Al\(_{\text{Si}}\)-O\(_{\text{i}}\) complex. Our result reveals that the total energy of configuration named \{a-Al\(_{\text{Si}}\), 2O\(_{\text{i}}\}\} shown in Fig. 7-1(c) is 1.66 eV less than that of the configuration named \{b-Al\(_{\text{Si}}\), 2O\(_{\text{i}}\}\} shown in Fig. 7-1(d). The total energies of these two different complexes are listed in Table 7.1. Therefore, an Al\(_{\text{Si}}\) atom prefers at the nearest site of an O atoms, while a B\(_{\text{Si}}\) atom favors the second nearest site of an O atom.

The different trend could be explained by the different electronegativity of Al and B elements, Al element has a stronger metalliclicity than B element. Therefore the direct Al-O bonding is energetically more favorable than the direct B-O bonding. The total density of state (TDOS) of the two Al\(_{\text{Si}}\)-O complexes shown in Fig. 7-1(c) and (d) are given in Fig. 7-3(a) and 7-3(b), respectively. It is seen that the two Al\(_{\text{Si}}\)-O complexes are shallow donors and no deep gap state are observed. The behavior of shallow donor can be easily understood because these Al\(_{\text{Si}}\)-O complexes include the O ring configuration. Each O ring is a double shallow donor, which donates two electrons to the Al\(_{\text{Si}}\) atom. As a
result, the \{\text{Al}_{\text{Si}}, 2\text{O}_{\text{i}}\} complexes are single shallow donors. It was reported that the stable \{\text{a-B}_{\text{Si}}, 2\text{O}_{\text{i}}\} configuration create deep level of 0.45 $eV$ below the CBM of bulk Si [120]. However, our results indicated that both \{\text{a-Al}_{\text{Si}}, 2\text{O}_{\text{i}}\} and \{\text{b-Al}_{\text{Si}}, 2\text{O}_{\text{i}}\} are shallow donors. Therefore, unlike \text{B}_{\text{Si}}-\text{O} defect complexes, \text{Al}_{\text{Si}}-\text{O} defect complexes do not introduce deep gap state and therefore they are not responsible for the reduction of carrier lifetime observed in Al and O co-existed Si.

### 7.3.3 \text{Al}_{\text{i}} and \text{O}_{\text{i}} in Si

The structures of \text{Al}_{\text{i}} and \text{O}_{\text{i}} complexes are depicted in Fig. 7-1(f) \{\text{a-Al}_{\text{i}}, 2\text{O}_{\text{i}}\}, (g) \{\text{b-Al}_{\text{i}}, 2\text{O}_{\text{i}}\} and (h) \{\text{c-Al}_{\text{i}}, 2\text{O}_{\text{i}}\}. The structures of \{\text{b-Al}_{\text{i}}, 2\text{O}_{\text{i}}\} and \{\text{c-Al}_{\text{i}}, 2\text{O}_{\text{i}}\} are constructed based on the B-O complexes reported by Sanati and Esteicher\textsuperscript{11}. We find that the new structure of \{\text{a-Al}_{\text{i}}, 2\text{O}_{\text{i}}\} shown in Fig. 7-1(f) has a lower energy than the configurations of \{\text{b-Al}_{\text{i}}, 2\text{O}_{\text{i}}\} and \{\text{c-Al}_{\text{i}}, 2\text{O}_{\text{i}}\}. Typically, an Al atom in Si prefers energetically a substitutional site rather than an interstitial site, because the formation energy of an \text{Al}_{\text{i}} is much higher than that of an \text{Al}_{\text{Si}}. Therefore, the concentration of \text{Al}_{\text{i}} atoms is typically much lower than that of \text{Al}_{\text{Si}} atoms. However, the situation changes significantly when both Al and O atoms are available because Al atoms bind O atoms forming Al-O complexes shown in Figs. 7-1(f), 7-1(g), and 7-1(h). The calculated TDOS of the three different configurations of \text{Al}_{\text{i}}-2\text{O}_{\text{i}} defect complexes are shown in Fig. 7-2(c)-(e). We find that the configuration of \{\text{a-Al}_{\text{Si}}, 2\text{O}_{\text{i}}\} shown in Fig. 7-1(f) introduces obvious deep levels in the band gap of Si, as indicated by the red arrow in Fig. 7-3. However, other two configurations shown in Fig. 7-1(g) and (h) do not show clear deep
gap stats, which is consistent with the previous work that predicts the shallow-donor feature of B\textsubscript{r}2O\textsubscript{r} defect complexes with the same structures [120].

**Figure. 7-2:** Calculated band structures of supercells containing (a) \{Si\textsubscript{64}\}, (b) \{Si\textsubscript{64}, O\textsubscript{i}\}, and (c) \{Si\textsubscript{64}, 4O\textsubscript{i}\}.
Figure 7-3: Calculated TDOS of supercells with various Al-O complexes.

To understand the origin of the deep gap state of \{a-Al, 2O_{\text{i}}\} complex shown in Fig. 2(f), we have calculated the band structures for supercells containing an individual Al_{\text{i}} and a \{a-Al_{\text{i}}, 2O_{\text{i}}\} complex. As shown in Fig. 7-4, the deep levels (indicated by the
arrows) introduced by the individual Al\textsubscript{i} atom and the \{a-Al\textsubscript{i}, 2O\textsubscript{i}\} complex are very similar, indicating that the deep level created by the \{a-Al\textsubscript{i}, 2O\textsubscript{i}\} complex is also due to the Al\textsubscript{i} atom in the complex. The calculated ionization energy for the \{a-Al\textsubscript{i}, 2O\textsubscript{i}\} complex is about 0.466 eV based the equation (1). The calculated partial charge densities associated with the deep gap states are given as the inserts in Fig. 7-4. It is seen that at both cases, the partial charge densities located around the Al\textsubscript{i} atoms, confirming that the deep gap states are originated from the Al\textsubscript{i} atoms. Compared with the configuration of complex \{a-Al\textsubscript{i}, 2O\textsubscript{i}\}, the structural characters of complexes \{b-Al\textsubscript{i}, 2O\textsubscript{i}\} and \{c-Al\textsubscript{i}, 2O\textsubscript{i}\} are very different. Complexes \{b-Al\textsubscript{i}, 2O\textsubscript{i}\} and \{c-Al\textsubscript{i}, 2O\textsubscript{i}\} have the split interstitial Al\textsubscript{i} configuration, in which the Al atom is at the substitutional site the Si is pushed to the interstitial site (Si\textsubscript{i}). Therefore, the Al atom does not introduce deep gap states. Because the s-orbit of Si is much lower in energy than the s-orbital of Al, the defect levels created by the Si\textsubscript{i} is much lower in energy than that created by Al\textsubscript{i}. Therefore, the levels created by complexes \{b-Al\textsubscript{i}, 2O\textsubscript{i}\} and \{c-Al\textsubscript{i}, 2O\textsubscript{i}\} are inside the valence band of Si and no gap states are observed.
7.3.4 The Effects of O Chemical Potential

We now discuss how the formation of the Al-2O\textsubscript{i} complexes may be influenced by the O chemical potentials. It is known that without O, an Al atom favors substitutional site and act as the shallow acceptor. An individual Al\textsubscript{i} atom is expected to have much higher formation energy than Al\textsubscript{Si}. However for Al-2O\textsubscript{i} complexes, their formation energies depend also on the chemical potentials. As indicated by equation (2), the formation energies of Al-2O\textsubscript{i} complexes should decrease as the chemical potential of O
increases. Therefore, the formation energies of Al\textsubscript{i}-2O\textsubscript{i} complexes could be lower than that of an Al\textsubscript{i}. If the high density of the \{a-Al\textsubscript{Si}, 2O\textsubscript{i}\} complex is formed, the carrier lifetime will be reduced due to the deep gap states created by the \{a-Al\textsubscript{Si}, 2O\textsubscript{i}\} complexes. Fig. 7-5 shows the calculated formation energies for various complexes as a function of the O chemical potential. The chemical potentials of Al and Si are obtained from the chemical potential of their corresponding bulk. It is seen that the formation energies of Al-O complexes depends strongly on the atomic chemical potential of O. As the O chemical potential increases, the formation energies of the Al-O complexes decrease quickly. For the complexes with more O atoms, the formation energies decrease even more. However, the formation energy of the individual Al\textsubscript{i} does not depend on the O chemical potential. As a result, at O-rich conditions, the formation energy of the \{a-Al\textsubscript{Si}, 2O\textsubscript{i}\} complex that creates deep gap states can be significantly lower than that of Al\textsubscript{i} and become comparable to that of Al\textsubscript{Si}. Therefore, O will assist the formation of Al-O defect complexes including the \{a-Al\textsubscript{Si}, 2O\textsubscript{i}\} complex. Our results therefore suggest that the formation of \{a-Al\textsubscript{Si}, 2O\textsubscript{i}\} complexes could be the reason why when Al and O coexist, the minority carrier lifetime of Si is reduced significantly.
7.4 Conclusion

Using first-principles DFT calculations, we have studied the structure and electronic properties of Al-O complexes in Si. Due to their different electronegativity, Al and B form different configurations when they combine with O atoms. We found that the \{a-Al_{Si}, 2O_{i}\} complex produces deep levels in the band gap of Si. The co-existence of O promote the formation of all Al-O related complexes including the \{a-Al_{Si}, 2O_{i}\} complex. Our results suggest that the formation of this Al-O complex could be
responsible for the experimentally observed carrier life reduction of Si when Al and O co-exist.
Chapter 8

Overall Conclusion

In this thesis, we comprehensively study structural properties, electronic properties and optical properties of the existing and potential solar cell absorbers, such as perovskites, Cu-based compounds and silicon. For a given material, we study the system symmetry and stability of different phases, and identify the formation energies of different defects in each phase using VASP. We also study the electronic properties, such as density of states, charge densities and band structures with respect to the crystal structure, and deduced the corresponding optical properties. Based on those properties, we calculate the optical absorption, and predicted the maximum efficiency of different PV materials.

We first showed that the distinguished defect physics of CH$_3$NH$_3$PbI$_3$ exhibits make it an excellent for solar photovoltaic applications: we showed that defects with low formation energies create only shallow levels, whereas defects with deep levels have high formation energies. In addition, the conductivity of CH$_3$NH$_3$PbI$_3$ can be varied from good $n$-type to intrinsic and to good $p$-type by cautiously controlling the growth conditions. We find that the unusual defect properties are originated from the strong I $p$ orbital and Pb lone-pair $s$ orbital antibonding coupling and the high ionicity of CH$_3$NH$_3$PbI$_3$. Our
results show that control of the growth condition is very important to fabricate high efficiency thin-film solar cells based on the halide perovskite absorbers.

We also have studied the extrinsic doping properties of CH$_3$NH$_3$PbI$_3$ perovskite with group-IA, -IB, -IIA, -IIIB, -IIA, -VA, and –VIA elements. We found that MAPbI$_3$ perovskite may be doped more easily into $p$-type than $n$-type by extrinsic dopants. Our results suggest that good $p$-type MAPbI$_3$ may be produced by doping with external elements including Na, K, Rb, Cu and O at I-rich/Pb-poor growth conditions. Group-IIA elements can produce shallow donor levels, but they cannot lead to good $n$-type CH$_3$NH$_3$PbI$_3$ due to the formation for neutral defects and compensation from intrinsic point defects. Our results imply that non-equilibrium growth conditions may be needed to dope MAPbI$_3$ for good $n$-type conductivity.

We do the similar research on another perovskite system, CH$_3$NH$_3$PbBr$_3$. Our calculations show that despite a large band gap, the dominant defects in CH$_3$NH$_3$PbBr$_3$ create only shallow levels, too. These special defect properties explain partially why CH$_3$NH$_3$PbBr$_3$–based solar cells are able to achieve high $V_{OC}$’s. We have further shown that the photovoltaic properties of CH$_3$NH$_3$PbBr$_3$–based perovskite absorbers can be tuned via defect engineering. CH$_3$NH$_3$PbBr$_3$ with low carrier concentration, i.e., required for good solar cell absorbers, can be grown under moderate growth conditions. Under Br-rich/Pb-poor growth conditions, highly conductive $p$-type CH$_3$NH$_3$PbBr$_3$ films are expected, which may be used as low-cost hole transporting materials for the lead halide perovskite solar cells. We have further indicated that $n$-type CH$_3$NH$_3$PbBr$_3$ should be produced through post-deposition diffusion of alkaline or alkaline earth metal ions.
Copper based Cu-V-VI compounds are one of the potential PV absorbers because of the low cost elements, various band range and good optical properties. Firstly, we systematically studied the structural, electronic, and optical properties of Cu$_3$-V-VI$_4$ compounds using first-principles DFT with the HSE06 hybrid functional. We found that Cu$_3$PS$_4$ and Cu$_3$PSe$_4$ prefer energetically the enargite structure, whereas other compounds are more likely in the famatinite structure. Considering the small energy differences (< 5 meV/atom) among the compounds with different structures, a large variety of phases may exist. The enargite Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ have bandgaps of 1.32 and 1.34 eV, respectively. Famatinite Cu$_3$PSe$_4$ and Cu$_3$AsS$_4$ have bandgaps of 1.31 and 1.15 eV, respectively. These materials are suitable for the applications in single junction photovoltaic solar cell. Cu$_3$PS$_4$ has a bandgap of 2.51 eV in the structure of enargite and 2.42 eV in the structure of famatinite. Cu$_3$SbS$_4$, Cu$_3$AsSe$_4$, and Cu$_3$PTe$_4$ have bandgaps in the range of 0.4 eV – 0.9 eV. These materials can be used as the absorbers for the top and bottom cells in the triple junction tandem cells.

Considering the better candidates as the new potential PV absorber materials, we also study the chalcostibite CuSbS$_2$. The chalcogenide structure with high symmetric ACh$_4$ unit should behave the good properties for the PV application. Interestingly, the lone pair dispersive s state of Sb atom plays an important role in the chalcostibite system. The higher Cu/V ratio in chalcogenide structure localizes the bands near CBM and leads to an increase in the DOS for transition, and subsequently enhances the corresponding absorption. The lone pair s of chalcostibite structure brings the void separation between SbS$_5$ units and form the bond-edge sharing structure externally. So the intrinsic electronic properties will behave unusually corresponding to the structural characteristics, where
CBM becomes less dispersive and offers the high density of states for the good absorption. In addition, the intrinsic doping situations are very different compared with the Cu$_3$SbS$_4$ system due to their structural distortions after doping.

Individual aluminum and oxygen are the benign elements for the silicon industry. However, the experimental observation shown that the carrier life is reduced when oxygen and aluminum co-exist. For knowing the physics behind this phenomenon clearly, we studied the structure and electronic properties of Al-O complexes in Si using first-principles DFT calculations. We found that Al and B form different configurations when they combine with O atoms because of their different electronegativity. Our results show that the $\{a-$Al$_{Si}, 2O_i\}$ complex produces deep levels in the band gap of Si. The co-existence of O promotes the formation of all Al-O related complexes including the $\{a-$Al$_{Si}, 2O_i\}$ complex.
References


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