Photovoltaic properties of metal-free semiconductor DMEDA·I₆: A first-principles investigation

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Abstract

Metal-free halide materials have garnered significant attention. However, because of their large band gap, current metal-free materials are not suitable as solar cell absorbers. A metal-free semiconductor, DMEDA·I₆, with a narrow band gap (∼1.36 eV) and strong light absorption, is a promising candidate for solar cell absorbers. Using the first-principles calculation method, a systematic investigation was conducted on the photovoltaic properties of DMEDA·I₆, including electronic properties, variation trend of the band gap under strain, defect physics, and band alignments of solar cell interfaces. It was found that DMEDA·I₆ crystallized in a one-dimensional I chain with alternating long and short I–I bond lengths. Although both the valence band maximum and conduction band minimum of DMEDA·I₆ are derived from the I p states, their compositions are distinguishable owing to the abnormal I–I bond arrangement. The band gap of DMEDA·I₆ increases when the lattice volume expands, which is similar to that of the popular lead-based perovskites and opposite to that of the conventional zincblende semiconductors. Among the intrinsic defects, only defect V₁ can produce a deep defect level in the band gap. The formation of V₁ can be suppressed under the I-rich preparation conditions; thus, I rich condition is proposed when preparing DMEDA·I₆ solar cell absorbers. Commonly used hole transportation materials are suitable for DMEDA·I₆-based solar cells, whereas electron transport materials (ETMs) with a lower lowest unoccupied molecular orbital than commonly used ETMs should be used.

1. Introduction

In the study fields of ferroelectrics [1], dye-sensitized solar cells [2, 3], electrocatalysts [4, 5], and nonlinear optics [6], metal-free materials have garnered significant attention owing to their advantages [1, 2] such as light weight, cost effectiveness, mechanical flexibility, high structural tunability, and ease of preparation. To the best of our knowledge, attempts to fabricate metal-free solar cells date back to as early as 1979 [7]. However, the previously reported [8–10] metal-free solar cells (all-organic solar cells) do not perform well and they have gradually lost their popularity. To date, the related progress has no additional breakthroughs. One of the main reasons for this is that no suitable metal-free absorber is present. In recent years, as halide organic-inorganic hybrid perovskites have become increasingly popular [11–13], metal-free halide materials have garnered significant attention [1, 14]. However, owing to the absence of metal ions, these reported metal-free organic-inorganic hybrid materials are generally wide band gap insulators, which are unsuitable for light absorption. Recently, a metal-free polyiodide (DMEDA·I₆), with a narrow band gap (1.36 eV) nearly approximate to the optimal band gap (1.4 eV), for light absorption was discovered [15]. The absorption coefficient was determined to be greater than 10⁴ cm⁻¹. Therefore, DMEDA·I₆ is a promising metal-free solar cell absorber. In a previous study, DMEDA·I₆ was identified as a promising optical detection material [15], but its photovoltaic properties are still unclear. A systematic study on the photovoltaic properties of DMEDA·I₆ will help improve the performance of DMEDA·I₆ solar cells.
In this study, by performing first-principles calculations, a systematic investigation was conducted on the photovoltaic properties of the metal-free semiconductor DMEDA-I_{6}. There are observations that DMEDA-I_{6} shows a one-dimensional I chain structure with alternating long and short I bond lengths. The upper valence bands are attributed to the antibonding states of the long I bonds and the bonding states of the short I bonds. The lower conduction bands comprise the antibonding states of the short I bond. The band gap of DMEDA-I_{6} increases when the lattice volume expands, and its variation trend is opposite to those of the conventional zincblende semiconductors, but the similar to those of popular perovskites. Among the intrinsic point defects, only I vacancies (V_{I}) produce a deep defect level in the band gap, which can act as a carrier non-radiative recombination center. Because I-rich conditions can suppress the formation of V_{I}, this condition is suitable to prepare DMEDA-I_{6}, which works as a solar cell absorber. The band alignments between DMEDA-I_{6} and commonly used hole transporting materials (HTMs) along with commonly used electron transporting materials (ETMs) demonstrate that the frequently used HTMs such as P3HT, CuI, NiO PTAA, and Spiro are all suitable for DMEDA-I_{6}-based solar cells, but an ETM with a lower lowest unoccupied molecular orbital (LUMO) is proposed as an alternative.

2. Calculation methods

All first-principles calculations were performed based on the density functional theory with the standard frozen-core projector augmented-wave [16, 17], as implemented in the vasp package [18, 19]. A 2 × 2 × 2 k-point grid mesh was used for the 2 × 2 × 1 supercell to simulate defects. A 400-eV cut-off energy for basic functions was set, and the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) [20] was used for the exchange-correlation functional. All the lattice parameters and atomic coordinates were fully relaxed until the force on each atom was less than 0.01 eV Å^{-1}. To accurately estimate the band gap, a hybrid functional known as HSE06 [21, 22] was used. Because there are no metal ions in the semiconductor, the effect of spin–orbit coupling (SOC) on the band gap value is negligible. The SOC was not considered in this study.

3. Results and discussions

The atomic structure [15] of DMEDA-I_{6} is shown in figure 1(a). In a unit cell, there are four symmetrically equivalent I–I–I units that are arranged in parallel along the ‘a’ direction, and the DMEDA molecules fill the cavity while lying in parallel, also along the ‘a’ direction. Accordingly, DMEDA-I_{6} appears as a one-dimensional (1D) chain-like atomic configuration. For more details, the bottom I–I–I unit was selected as a representative, as shown in figure 1(b). The fully relaxed bond lengths of I_{1}–I_{2}, I_{2}–I_{3}, and I_{3}–I_{4} are 3.3 Å, 2.88 Å, and 3.3 Å, respectively (The values correspond with experimental results [15] of 3.37 Å and 2.78 Å for long and short I–I bonds, respectively), which demonstrates that the I chain exhibits an alternating long and short bond length configuration. As reported in previous studies [15], along (‘a’ direction in figure 1(a)) and perpendicular (‘b’ and ‘c’ directions in figure 1(a)) to the I chain, DMEDA-I_{6} exhibits a strong anisotropy character on optical absorption and carrier transportation. The optical absorption (∼10^{6} cm^{-1}) along the I chain direction is three

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**Figure 1.** (a) Atomic structure of DMEDA-I_{6}. The C, N, H, and I atoms are denoted by brown, silver, white, and red balls respectively. (b) Bottom I–I–I unit in (a). Fully relaxed I–I–I bond length values are shown, and the dashed line denotes the bond between I_{1} and the adjacent I in the next period unit (I_{1}).
orders of magnitude stronger than that along the direction perpendicular to the I chain. Similarly, the carrier effective mass along the I chain is two orders of magnitude smaller than that along the direction perpendicular to the I chain. Because both high light absorption and effective carrier transportation are the requirements for an excellent solar cell, when fabricating DMEDA-I₆ solar cells, emphasis should be put on proper sample growth orientation.

In popular lead–based perovskites, intrinsic defects only produce shallow and embedded defect levels, enabling lead–based perovskite defect tolerance [23, 24]. Defect tolerance is deemed to originate from a specially inverted band structure in which the valence band maximum (VBM) is composed of anti-bonding hybridization between metal s and halogen p [23, 25]. However, metal-free DMEDA-I₆ does not contain metal ions, and both the VBM and conduction band minimum (CBM) are composed of I-p states [15], which are different from those of perovskites. Figures 2(a) and (b) show the partial charge densities of the VBM and CBM for DMEDA-I₆, respectively. It can be observed that the VBM is composed of I₁–I₂ (short I–I bond) bonding hybridization states along with I₁–I₂ (long I–I bond) anti-bonding hybridization states, whereas the CBM is purely formed by anti-bonding hybridization states of I₁–I₃ (short I–I bond), and it has no contributions from I₁–I₂ bond (long I–I bond) states.

In the architecture of a solar cell device, lattice mismatch between adjacent layers can enforce stress on the material near interfaces. The stress on the absorber directly changes the lattice parameters to change the band gap and influence the light harvesting performance. Figure 3 shows the calculated band gap variation depending on the strain of DMEDA-I₆, along with the conventional zincblende CdTe and popular perovskite CsPbI₃ for comparison. Because this study only focuses on the change dependence, the band gap values in figure 3 were calculated using the PBE functional. To describe the strain quantitatively, we define \( \gamma = \frac{a - a_0}{a_0} = \frac{b - b_0}{b_0} = \frac{c - c_0}{c_0} \)

where \( a_0, b_0, \) and \( c_0 \) are the equilibrium lattice parameters, and \( a, b, \) and \( c \) are the changed lattice parameters under strain. From this definition, \( \gamma < 1 \) denotes lattice compression, whereas \( \gamma > 1 \) denotes lattice expansion. As shown in figure 3, when the lattice expands, the band gap of DMEDA-I₆ increases, which is the same as that of CsPbI₃, but opposite to that of the conventional zincblende CdTe. This can be understood from the composition of the band edges, as shown in figure 2. When the lattice expands, the distances of I₁–I₂ and I₁–I₃ become significantly larger (up to 13%), whereas the distance of I₂–I₃ changes insignificantly (less than 1%). Therefore, the band edge shift contributed by the I₁–I₂ bond (short I–I bond) is negligible. Because the CBM is mainly composed of the anti-bonding I₁–I₃ states, the CBM shift makes an insignificant contribution to the band gap variation. In the case of VBM shift, the antibonding character of I₁–I₂ and I₁–I₃ contributing to the composition of the VBM makes the VBM push down when the bond lengths of I₁–I₂ and I₁–I₃ increase. Therefore, the abnormal variation trend of the band gap for DMEDA-I₆ originates from the antibonding component of VBM. A similar reason is understandable for CsPbI₃, whose VBM also has an anti-bonding character. Hence, despite the absence of metal ions, DMEDA-I₆ exhibits the same variation trend of the band gap under strain as those of popular perovskites.

The formation energy \( \Delta H_f(\alpha,q) \) of a defect \( \alpha \) in the charge state \( q \) is a function of the Fermi energy and atomic chemical potentials, which can be described as follows [26–28]:

![Figure 2. Partial charge density of the VBM (a) and CBM (b).](image-url)
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\Delta H_f(\alpha, q) = E(\alpha, q) - E(\text{host}) + \sum n_i[\mu_i + E(i)] + q(E_F + E_{\text{VBM}}).
\]

where \(E(\alpha, q)\) and \(E(\text{host})\) denote the total energies of the supercell with a defect \(\alpha\) in charge state \(q\) and the host, respectively. Term \(n_i\) denotes the number of atoms that change when the corresponding defect forms. Term \(\mu_i\) denotes the atomic chemical potential referring to the total energy \(E(i)\) of the bulk. Term \(E_F\) denotes the Fermi energy referencing to VBM, which ranges from 0 to the band gap value, and \(E_{\text{VBM}}\) denotes the VBM energy. The charge transition level of a defect is defined as the Fermi energy when the formation energies of the defect in two different charge states are equal.

Using equation (1), the formation energies of possible intrinsic point defects such as I vacancy (VI), I interstitial (I_i), ME (DMEDA molecule) vacancy (V_{ME}), I, and ME antisite (IM_{ME}) as a function of Fermi energy under I-rich (figure 4(a)) and ME-rich (figure 4(b)) conditions were determined. The charge transition levels for each defect were denoted by the turning points on the formation energy curve. Because of the significantly larger ion size of ME than that of I, replacing I with ME is inappropriate; therefore, replacing I with ME is excluded. Although there are three non-equivalent I sites, as shown in figure 1(b), the formation energy curves of VI at the three non-equivalent I sites are almost coincident; hence, only one VI is displayed in figure 4.

As observed in figure 4, all defects are in an ionized state throughout the band gap range. When the Fermi energy moves from the VBM to the CBM, the formation energies of acceptors such as V_{ME} and IM_{ME} decrease, whereas those of the donors such as I_i increase. Under I-rich conditions, V^2_{ME} has the lowest formation energy among all defects, wherever the Fermi energy is located in the band gap. As shown in figure 4, when the Fermi energy is less than 0.6 eV, V_{I} is ionized in the +1 charge state. When the Fermi energy moves beyond 0.6 eV to CBM, the ionization state of V_{I} transforms from +1 to −1. This demonstrates that when the Fermi energy is less than 0.6 eV, V_{I} exhibits donor behavior, but when the Fermi energy is greater than 0.6 eV, V_{I} exhibits accepter behavior. Another particular defect is I_{i}. In conventional ionic halide semiconductors, I_{i} defects are usually regarded as acceptors, whose defect level is usually located near the VBM, and they prefer to capture one electron ionized into the −1 charge state. However, as observed in DMEDA·I_{6}, I_{i} is more likely to lose electrons and act as a donor.

Under ME-rich conditions, the formation energies of acceptors such as IM_{ME} and V_{ME} significantly increase, whereas the formation energy of donor I_{i} decreases. In this case, V_{I} has a more rapid decrease in formation energy and becomes dominant among all the defects. V_{I} can generate a +1/−1 transition level at 0.6 eV above VBM in the middle of the band gap, which could act as a non-radiative recombination center and damage solar cell performance. Hence, the ME-rich condition should be avoided when preparing the DMEDA·I_{6} absorber.

In solar cell architecture, the most important interfaces are the HTM/absorber and absorber/ETM. The HTM/absorber interface is used to block electrons and transport holes, whereas the absorber/ETM interface is used to extract electrons [29, 30]. Therefore, the highest occupied molecular orbital (HOMO) of the HTM is required to be higher than the VBM of the absorber, whereas the LUMO of the ETM should be lower than the
CBM of the absorber. A reasonable option for HTM and ETM is crucial for achieving excellent solar cell performance. In perovskite solar cells, the commonly used HTMs are P3HT, CuI, NiO, PTAA, and Spiro, and commonly used ETMs are ICBA, TiO2, ZnO, SnO2, PCBM, and C60 [29, 31, 32]. To obtain their band alignments with DMEDA·I6, the absolute VBM and CBM energies of DMEDA·I6 with reference to the vacuum level were first determined, and the absolute HOMO and LUMO of the other popular lead-based perovskites, along with the HTMs and ETMs, were extracted from experimental reports. To calculate the absolute VBM energy of DMEDA·I6, the present study used a slab model with sufficient layers in the (100) orientation (two I−I−I− unit layers) and a 20-Å vacuum layer to obtain the potential difference between the bulk and vacuum. After the absolute VBM energy is determined, the absolute CBM energy is directly obtained by adding the experimental band gap value (1.36 eV) to the absolute VBM value.

Figure 5 displays the calculated band alignments between DMEDA·I6 and commonly used HTMs and ETMs, as well as the popular perovskites CsPbI3 and CsPbBr3, the latter three of which were extracted from experimental reports [29–32]. The VBM of DMEDA·I6 is lower than that of all commonly used HTMs, whereas the CBM of DMEDA·I6 is lower than that of all commonly used ETMs. Therefore, the commonly used HTMs are all suitable for DMEDA·I6 solar cells, whereas the commonly used ETMs are unsuitable. Hence, when fabricating DMEDA·I6 solar cells, the commonly used HTMs such as P3HT, CuI, NiO, PTAA, and Spiro, can also be used, but ETMs with a relatively lower LUMO should be an alternative.

4. Conclusions

DMEDA·I6 is a promising metal-free solar cell absorber. Through first-principles calculations, the photovoltaic properties of DMEDA·I6 were systemically investigated. Although both the VBM and CBM of the metal-free halide DMEDA·I6 are derived from I p states, their compositions are different because of the abnormal I–I bond arrangement in the 1D I-chain structure. The band gap of DMEDA·I6 increases when the lattice volume expands, which is the same as that of the popular halide perovskites, but opposite to that of the traditional zincblende semiconductors. Among intrinsic point defects, only V I produces a deep level in the band gap, which can act as a carrier non-radiative recombination center. Because I-rich preparation conditions can suppress the formation of V I-rich conditions have been proposed for the preparation of the DMEDA·I6 absorber. When fabricating DMEDA·I6-based solar cells, commonly used HTMs such as P3HT, CuI, NiO, PTAA, and Spiro, are also suitable, but ETM with a lower LUMO than that of the commonly used ETMs should be an alternative. Based on these results, further studies will focus mainly on two directions. First, a suitable ETM for the DMEDA·I6 solar cell should be determined. Second, proper impurity doping can be attempted to enhance the adjustment of the defect physics.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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