First-principles calculation of the optoelectronic properties of doped methylammonium lead halide perovskites: A DFT-based study

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ABSTRACT

Methylammonium lead halide perovskites have emerged as an exciting material for research by virtue of their attractive optoelectronic properties and easy fabrication techniques leading to their use in optical devices, especially solar cells. An extensive knowledge of these properties along with a study of how they can be potentially tuned to suit requirements and improve the efficiency of devices is imperative in the realization of the full potential of these materials. In this regard, we present first-principles modeling and analysis of lead halide organometallic perovskites to determine their optoelectronic properties using density functional theory. Upon validating our model parameters by comparing the calculated optical constants and bandgaps of pure methylammonium lead halide perovskites with published experimental data, we extended the analysis to perovskites doped with various percentages of halogen atoms. We have determined the values of refractive index and extinction coefficient at different doping concentrations for a wide range of photon energies, establishing a comparison between them. In addition, we have investigated the variation in the bandgap and the effective mass of charge carriers with changes in doping concentration. We have also presented the effect of incorporating spin–orbit coupling on the band structure calculations. Our results show a significant reduction in the calculated value of the bandgap and also substantial changes in the values of effective mass upon incorporation of spin–orbit coupling. The data presented in this paper highlight the favorable optoelectronic properties of methylammonium lead halide perovskites and demonstrate the trends in these properties upon halogen doping, thereby facilitating the realization of perovskite-based high-performance solar cells, lasers and other optoelectronic devices with improved efficiency.

1. Introduction

Organic-inorganic lead halide perovskites, $CH_3NH_3PbX_3$ (X = Cl, Br, I), (hereafter referred to as $MAPbX_3$, where MA represents methylammonium), have propelled great research interest due to their attractive optoelectronic properties and simple, low-cost fabrication processes leading to their applications in solar cells, photodetectors, lasers, and light-emitting devices [1,2]. Optical and electrical properties of lead halide perovskites can also be tuned to suit application requirements by altering the chemical composition of halides, metal, and/or cation [3–5]. $MAPbX_3$ was first introduced in 2009 as a dye-sensitized photovoltaic cell material which achieved a power conversion efficiency (PCE) of 3.8% [6]. Since then, numerous research endeavors have been undertaken in pursuit of higher efficiency solar cells, such as changing the chemical composition of $MAPbX_3$ by doping of the halogen atom or replacing the MA-group [7–9]. Bandgap engineering by incorporating bromine into $MAPbI_3$ (i.e. $MAPb(I_{1-x}Br_x)_3$) enabled broadband solar spectrum to be covered resulting in solar cells with an efficiency of 12.3% [10]. Absorber with chlorine doped $MAPbI_3$ has also been reported to have a much higher PCE (17.91%) [11]. Further, solution deposited mixed halide perovskite ($MAPbI_{3-x}Cl_x$, a mixture of CH_3NH_3I and $PbCl_2$) has also yielded an impressive efficiency of 19.3% [12]. These works show the immense potential of doped perovskites where doping has significantly enhanced the PCE. In this regard, a comprehensive knowledge of the material properties is integral to the design of optoelectronic devices. In particular, values of the refractive index (n) and extinction coefficient (k) at different wavelengths are needed for analysis of optoelectronic devices. If the PCE of perovskite-based solar cells is to be improved even further, knowledge of the bandgap and complex refractive index of $MAPbX_3$ is essential, along with their variability and how they can be potentially altered or tuned. As such, considerable effort has been made in recent years to the accurate determination of these material properties. The refractive indices of pure $MAPbX_3$ (X = Cl, Br, I) have been experimentally determined, along with their bandgaps, by a number of research groups [13–23]. Several researchers have attempted to determine the effect of doping

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halogen atom on the resulting perovskite's refractive index and bandgap. The complex refractive index (and dielectric function) of a thin film of MAPbI$_{(3-x)}$Cl$_x$ was determined by variable-angle spectroscopic ellipsometry (VASE) in the range of 300–1100 nm [24]. The first-principles modeling of the mixed halide MAPbI$_2$X (X = Cl, Br) was carried out in 2013 and the bandgap of the resulting material was determined by a density functional theory (DFT) based *ab initio* derivation using the generalized gradient approximation (GGA) coupled with the exchange–correlation function proposed by Perdew–Burke–Ernzerhof (PBE) [25–27].

Despite extensive work on the determination of the optical constants and bandgaps of pure MAPbX$_3$, the material properties of doped/mixed halide perovskites have not yet been fully explored. As mentioned above, research groups have attempted to determine the optical constants and bandgaps of a few mixed halides, such as MAPbI$_2$Cl, MAPbICl$_2$, MAPbIBr$_2$ and MAPbI$_2$Br, where 1 halogen atom out of 3 had been replaced corresponding to a dopant atom concentration (defined as the number of dopant halogen atoms divided by the total number of halogen atoms in the system) of 33.33%. Even for these cases, *n* and *k* data for a wide range of photon energies not limited to the solar spectrum is still unavailable. Moreover, MAPbX$_3$ doped with Cl, Br or I (as appropriate) at doping concentrations intermediate between 0% and 33% have not been reported yet. The same applies to the values of bandgap and effective masses of doped MAPbX$_3$. Even for undoped halide perovskites, experimental data of refractive index show immense variations between values published by different research groups rendering it difficult to compare or extract a trend from them. For instance, a refractive index of approximately 3.2 for MAPbI$_3$ at 400 nm was measured in Ref. [20], which shows a 45.5% deviation from the value of 2.2 obtained in Ref. [23] at the same wavelength. A similar scenario is seen in MAPbBr$_3$ as well where, in Refs. [19 and [17], measurements of 2.26 and 2.46 respectively, for refractive index at 400 nm were obtained. Several factors may have contributed to these variations, for instance, different fabrication techniques (such as low-temperature solution processing [23] or sequential layer-by-layer deposition method [24]) may have been employed by different groups leading to material anisotropy. Even if similar techniques were used for fabrication, the resulting compounds may have variable grain sizes (leading to variable scattering rates) or may contain two-phase compounds (due to material degradation or production by-product) which could cause differences in measurements [21]. Thus, in this work, we have focused on the DFT-based first-principles modeling of MAPbX$_3$ and determination of its bandgap, carrier effective masses and optical constants (*n* and *k*) when doped with Cl, Br and I (as appropriate). We have determined the *n* and *k* curves of halogen-doped halide perovskites for percentages of dopant atoms between 3% and 33.33% and established a comparison between the data at each concentration. This doping profile was implemented on MAPbI$_3$ (doped with Cl and Br) and MAPbBr$_3$ (doped with I and Cl). We have also calculated the bandgap and effective mass of charge carriers at dopant percentages of 16.67% and 33.33% by including spin–orbit coupling (SOC) in the calculations and compared them with values obtained without SOC.

2. Simulation setup for DFT analysis

2.1. Geometry optimization and optical properties calculation

Density functional theory (DFT) [26,27] is one of the most versatile methods in computational material science for investigating the electronic structure of many-body systems. In this paper, to begin with, the crystal structures of pure MAPbX$_3$ [28] were geometry optimized using the GGA-PBE functional [29]. The suitability of this functional stems from the fact that the GGA-PBE optimized structures of perovskites have been shown to conform well to recorded experimental data [25,30,31]. We chose a $2 \times 2 \times 2$ k-point grid for geometry optimization. A 25 Ry (approx. 340 eV) plane-wave basis set cutoff has been

shown to produce accurate results for periodic GGA-DFT calculations on this material [25]. Nevertheless, we carried out tests on undoped MAPbI$_3$ using cutoffs ranging from 280 eV to 400 eV and observed no significant changes in the complex refractive index spectrum. Thus, a plane-wave basis set cutoff of 280 eV and a self-consistent field (SCF) tolerance of 2.0×10^{-6} eV/atom was chosen for subsequent simulations as it allowed a larger supercell structure to be simulated which in turn enabled the calculation of smaller doping concentrations. Electron-ion interactions were described by ultrasoft pseudopotentials [32]. The GGA-PBE functional was used in optical calculations, as previous works have shown its suitability in determining the optical constants of perovskites [25,33] and many other materials [34] in general. However, for optical calculations, the aforementioned k-point mesh proved to be insufficient as the optical matrix elements changed much more rapidly within the Brillouin zone than electronic energies themselves. Therefore, a separate and denser $5 \times 5 \times 5$ k-point mesh was chosen for optical simulations. Eight empty bands were considered and a band energy tolerance of 1.0×10^{-5} eV was implemented. The validity of these computational settings was further established by benchmarking simulated data with experimental works as shown in Section 3.

Calculations of optical properties were performed by first determining the complex dielectric constant of the material and using this expression to determine the complex refractive index. The relation between the complex dielectric function and complex refractive index is given by:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2, \tag{1}$$

where N is the complex refractive index represented by:

$$N = n + ik \tag{2}$$

The imaginary part of the dielectric constant is calculated from an expression similar to the Fermi's Golden Rule for time-dependent perturbations [35] (Eq. (3)).

$$\varepsilon_2(q \to O_{\hat{u}}, h\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{k,v,c} |\langle \Psi_k^c | u \cdot r | \Psi_k^v \rangle|^2 \delta(E_k^c - E_k^v - E), \tag{3}$$

where u is the vector that defines the polarization of the incident electric field, Ω represents the volume of the system, Ψ_k^v and Ψ_k^c define wavefunctions of the initial state of valence band and final states of conduction band, respectively. E_k^c and E_k^v are the general notations of the conduction and valence band energy levels and r is the space vector. The matrix elements of the position operator, represented in terms of the matrix elements of the momentum operator as well as a non-local potential is,

$$\langle \psi_k^c | r | \psi_k^v \rangle = \frac{1}{i\omega m} \langle \psi_k^c | P | \psi_k^v \rangle + \frac{1}{\hbar\omega} \langle \psi_k^c | (V_{nl}|r) \psi_k^v \rangle \tag{4}$$

where P and V_{nl} are the momentum and nonlocal potential, respectively. Since the complex dielectric function is a causal response, the real part of the dielectric function is subsequently calculated from the imaginary part using the Kramers-Kronig transform [36,37] before the complex refractive index is finally determined.

Geometry optimization, followed by optical property calculation, was carried out according to the aforementioned methodology on halide doped perovskites to obtain *n* and *k* values for doping concentrations and structures between 3% and 33.33%, as these have not yet been reported. A single MAPbX$_3$ unit cell contains 3 halogen atoms as shown in Fig. 1(a), whereas Fig. 1(b) and (c) represent structures expanded to form supercells containing 2 and 9 unit cells, respectively. Therefore, these structures contain $(2 \times 3 =)$ 6 and $(9 \times 3 =)$ 27 halogen atoms, respectively. Progressively increasing number of halogen atoms were then replaced from these structures with other halogen atoms to obtain increasing concentrations of dopant atoms. For example, replacing 1 atom of iodine in a 9 unit cell structure of MAPbI$_3$ resulted in a dopant atom concentration of $(1/27 = 0.0370)$ 3.7%. Similarly, replacing 2 and 3 iodine atoms resulted in dopant atom