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Electronic and gap properties of lead-free perfect and mixed hybrid halide perovskites: An *ab-initio* study

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ABSTRACT

Hybrid halide perovskites are currently under intense investigation due to their potential applications in optoelectronics and solar cells. Among them, $MAPbI_3$ where MA stands for the methylammonium cation, exhibits ideal properties for solar cells. In attempt to identify new lead-free halide perovskites we have studied using *ab-initio* electronic structure calculations in conjunction with hybrid functionals a series of $MABX_3$ compounds where B is a divalent cation and X is a halogen atom. Our results suggest that the compounds under study exhibit a variety of lattice constants and energy band gaps. Especially, $MAGeCl_3$ and $MAGeBr_3$ are susceptible to replace $MAPbI_3$ in devices since they show comparable energy gaps. Further calculations on the mixed hybrid halide perovskites show that we can tune the values of the energy gap although no simplified pattern exists. Our results pave the way for further investigation on the use of these materials in technology relevant applications.

1. Introduction

Renewable energy sources are essentially a one-way road for energy consumption in the 21st century, since the finite and limited supply of fossil fuels is bound to come to an end. The sun is a practically infinite energy source, and photovoltaic (PV) devices that turn the energy of sunlight into electricity are expected to become more prominent as a main renewable energy source [1]. Silicon is the most widely used material in solar cell technology, with a history of over 60 years [2]. Other types of solar cells used in PV technology include type III-V semiconductors, quantum dots, dye-sensitized solar cells, organic solar cells and perovskites.

Designated as perovskite is a material that has the general structure of ABX_3. The most known perovskites are the ones where X is an oxygen. To achieve charge neutrality in that case, A has to be a cation of +2 valence and B a cation of +4 valence of dissimilar size like in $CaTiO_3$ [3]. The versatility of perovskites makes them highly attractive as they can form multidimensional structures pertaining to the same chemical formula through use of different combinations of various components [4,5]. A wide variety of elements may be incorporated in the ABX_3 structure, as long as the requirement for charge neutrality is satisfied. Although oxide perovskites are the most well-studied and widely used in applications due to their multifunctional nature, their wide band gaps limit their use in solar cell technology, as they utilize a mere 8–20% of the solar spectrum [3].

To overcome the poor absorption of the oxygen perovskites, other types have been proposed like the halide perovskites where the X anion is a halogen instead of oxygen and mainly the so-called hybrid or organometallic halide perovskites, where the A cation is an organic molecule [1,5–7], offering the ability to tune the photoconductive properties through varying halide components [8]. Their success is based on a highly favorable charge-carrier mobility so that both light absorption and charge conduction are possible [9]. One of the most widely used organic cations is methylammonium (MA) which has the chemical formula $CH_3NH_3^+$ [1]. Especially the one containing lead as the divalent cation and iodine as the halogen, $MAPbI_3$, has attracted most of the attention [10–12], and its growth conditions have been widely studied [13,14].

$MAPbI_3$ has an experimental gap of 1.5 eV, which makes it suitable for absorption in the optical regime [15]. More recent experimental results on cubic crystals of $MAPbI_3$ gave a value of 1.69 eV at 330 K [16]. Although several of its properties and their effect on the band gap have been widely studied, such as the influence of the orientation of the MA atoms [17–19], the toxicity of the lead atoms led to the search for alternative hybrid halide perovskites [20]. *Ab-initio* electronic structure calculations have been also employed in this search. Sn, which is isovalent to Pb, has been proposed as a replacement but it oxidizes very easily and the perovskite structure is destroyed [21,22]. Sr replacement for Pb in $MAPbI_3$ leads to an energy gap double the initial one and thus cannot be applied

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in PV applications [23]. The partial substitution of I atoms with other halogen influences the energy width of the band gap but does not solve the toxicity problem [24,25].

Motivated by the search for lead-free hybrid halide perovskites, we carry out an extended *ab-initio* study of the $MABX_3$ compounds. As X we have considered all possible halogen atoms, namely F, Cl, Br and I. Divalent B cations can be either the alkali earth elements (Ca, Sr, Ba) since they have two valence *p* electrons, the late transition metal atoms (Zn, Cd, Hg) which have two valence *s* electrons and the metalloids (Ge, Sn, Pb) which have also two valence *p* electrons but contrary to the alkali earth elements the valence *d* states are completely occupied. For all 36 resulting compounds we have relaxed the position of the atoms and the C—N bond length of the MA cation and determined the equilibrium lattice constants. For the equilibrium lattice constants, we have employed advanced functionals of the exchange and correlation energies and have determined the width of the energy band gaps. Finally, we have also studied the possibility to tune the energy band gaps in mixed hybrid halide perovskites by mixing two kinds of halogen atoms in the unit cell. In Section 2 we present the details of our calculations. Section 3 is devoted to the structural properties of the compounds under study and Section 4 to their electronic and gap properties. In Section 5 we present our results on the mixed compounds and finally in Section 6 we summarize and present our conclusions.

2. Computational method

We have calculated the structural and electronic properties of the hybrid halide perovskites under study employing the *ab-initio* total energy and molecular-dynamics program VASP (Vienna *Ab-initio* Simulation Package) developed at the Institut für Metaliphysik of the Universität Wien [26]. We made use of the projector augmented waves (PAW), which are a generalization of the ultrasoft pseudopotentials used in conventional pseudopotential electronic structure methods [27]. To account for the exchange-correlation potential we have used the generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhof (PBE) [28]. More precisely, we have employed the parametrization of PBE developed by Perdew et al. in Ref. [29] which restores the correct density-gradient expansion for the exchange energy in solids with respect to the initial PBE formalism (known in literature as PBEsol).

Although GGA in general is known to reproduce accurately the structural properties, it presents a serious drawback regarding semiconductor materials: while the calculated band structure is qualitatively correct, the energy gap is largely underestimated. But the exact value of the energy gap is crucial for applications since it determines the wavelength of the absorbed light. To restore the correct value of the energy gap several methods have been proposed. One of the most rigorous is the use of more complex functionals where the exchange energy is a mixture of the GGA and Hartree-Fock functionals. These functionals are known as "hybrid functionals" and the most well-known in materials science is the Heyd-Scuseria-Ernzerhof (HSE06) functional [30], which has been successfully implemented in VASP [31]. Except HSE06, we have also performed calculations using the modified Becke-Johnson functional in conjunction with the PBEsol one (known as mBJ+PBEsol). The mBJ has been developed in 2006 by Becke and Johnson in an attempt to provide an efficient exchange functional which would reach the accuracy of the hybrid functionals like HSE06 but which would need similar CPU resources like GGA [32] contrary to HSE06 based calculations which are very demanding. It became popular in 2009 when Tran and Blaha introduced it in the full-potential (linearized) augmented planewave and local orbitals [FP-(L)APW+lo] method and found that it gives band gaps for a series of insulators and semiconductors close to the HSE functionals [33]. We should also note that the mBJ functional, actually, is a potential-only functional being a local approximation to an atomic exact-exchange potential plus a screening term which is used in conjunction to one of the exchange-correlation schemes (PBEsol in our case). Thus the mBJ-based calculations within VASP are not self-consistent with respect to the total energy contrary to the HSE06 or PBEsol functionals (details are given in the online manual of VASP [34]).

We should also shortly discuss the accuracy of the various functionals to study the compounds of interest. Although calculations using HSE06 are expected to give more accurate results than the usual GGA functionals and mBJ calculations are expected to reach the accuracy of HSE06, in reality the success of the HSE06 and mBJ functionals is materials specific and it is established only when the computed values are compared to the experimental ones. HSE06 has been applied with success to the study of the electronic properties of the oxygen perovskites [35]. Moreover, recent experiments on cubic crystals of $MAPbI_3$ by Quarti and collaborators produced a value of 1.69 eV at 330 K [16]. As will be discussed in Section 4, PBEsol produces a value of 1.49 eV, while HSE06 and mBJ+PBEsol produce values of 1.82 eV and 1.85 eV, respectively. Since *ab-initio* calculations are carried out at 0 K and the width of the band gap drops with the temperature, we expect that our calculated HSE06 and mBJ+PBEsol band gap values are close to the experimental one. All the above provide strong evidence that HSE06 and mBJ+PBEsol are suitable to study the halide perovskites, although more experimental results on crystals are needed for definitive conclusions.

Concerning the details of the calculations, we have used for all of them a cutoff for the kinetic energy of the plane waves of 500 eV and for the Ge, Sn and Pb atoms we have included in the PAW basis the 3*d*, 4*d* and 5*d* orbitals, respectively, as valence states. For the case of the mBJ+PBEsol calculations we have used a more advanced basis set including also the kinetic energy density of the core electrons. In order to establish the accuracy of our calculations we have calculated $MAPbI_3$ as a test case, since it is the most studied compound in literature. The obtained results were in perfect agreement with the existing ones in literature [17], as will be discussed later.

3. Structural properties

The hybrid halide perovskites under study crystallize in a cubic structure shown in Fig. 1 [19]. The divalent cations sit at the corners of the cube surrounded by halogen atoms in an octahedral environment. The MA cation sits at the center of the cube. The first step in our study is the determination of the equilibrium lattice constant. To determine it for all the compounds we have performed total energy calculations for several lattice constants using a $6 \times 6 \times 6$ Monkhorst-Pack grid in the 1st Brillouin zone [36] in conjunction with the PBEsol functional. For each lattice constant we fixed the position of the divalent cation and the halogen atoms. We allowed the MA atom to fully relax within the cell (the positions of all C, N and H atoms have been allowed to change). The only constraint, which was imposed, was that the C—N bond stays parallel to the [1 0 0] direction passing from the center of the cube. In reality as shown in Ref. [19] the MA cations can rotate in very short times but such a picture cannot be captured by conventional electronic structure calculations. Moreover, test calculations for $MAPbI_3$ have shown that the orientation of the MA cation is not decisive for the obtained values of the band gap. We have chosen 7 values around the equilibrium and fitted a third order polynomial curve to determine the equilibrium lattice constant corresponding to the minimum of the energy. In Fig. 2 we show the calculated total energy values versus the lattice constants as well