Valence and conduction band tuning in halide perovskites for solar cell applications†

Simone Meloni,†a Giulia Palermo,§b Negar Ashari-Astani,‖a Michael Grätzelb and Ursula Rothlisberger*aa

We performed density functional calculations aimed at identifying the atomistic and electronic structure origin of the valence and conduction band, and band gap tunability of halide perovskites ABX3 upon variations of the monovalent and bivalent cations A and B and the halide anion X. We found that the two key ingredients are the overlap between atomic orbitals of the bivalent cation and the halide anion, and the electronic charge on the metal center. In particular, lower gaps are associated with higher negative antibonding overlap of the states at the valence band maximum (VBM), and higher charge on the bivalent cation in the states at the conduction band minimum (CBM). Both VBM orbital overlap and CBM charge on the metal ion can be tuned over a wide range by changes in the chemical nature of A, B and X, as well as by variations of the crystal structure. On the basis of our results, we provide some practical rules to tune the valence band maximum, respectively the conduction band minimum, and thus the band gap in this class of materials.

1 Introduction

Mixed organic/inorganic and fully inorganic halide perovskites of the formula ABX3 (A = organic or inorganic monovalent cation, B = bivalent cation, X = halogen anion) (see Fig. 1), have recently emerged as highly efficient light harvesting and charge carrier transport materials for solar cells.†–‡ Power Conversion Efficiencies (PCE), i.e. the percentage of solar light converted into electric current, as high as a certified 22.1% have been reported for perovskite based solar cells.⁴

Several strategies have been attempted to increase the PCE of halide perovskites, some targeting the quality of perovskite films, e.g. its uniformity⁴ and defect passivation,⁵ others focusing on the intrinsic optical and electronic properties, such as tuning of the band gap, \(E_g\). In the latter case, the objective is obtaining a compound with a band gap close to the ideal value of 1.3 eV.⁶ Seok and coworkers have shown that in mixed I/Br perovskites, ABX3–xBrx, \(E_g\) can be tuned by changing the halide composition, x.⁷ In particular, in methyl ammonium lead iodide/bromide perovskites, MAPbI3–xBrx (MA = methyl ammonium), the band gap widens with increasing x. It has also been shown that⁸ employing larger cations, which favor a more cubic-like structure, the band gap can be reduced. Different hypotheses have been put forward trying to explain the origin of band gap variation. Amat et al.¹² suggested the structural variations of the PbI framework (e.g. the X–B–X angle) as the main parameter determining the band gap and in particular justified the effect of larger cations with lower octahedral tilting angles. Filip et al.¹³ further investigated this idea and studied the band gap dependence as a function of the orientation of PbI octahedra in a Platonic orthorhombic PbI3 perovskite, i.e. an orthorhombic lead iodide perovskite in which the monovalent cations are replaced by a background charge. They have shown that rotating the octahedra around the equatorial and apical bond angles in the domain consistent with the other structural constraints it is possible to change the band gap in the range 1.1–1.9 eV. They have also shown that by changing the monovalent cation one can tune the orientation of PbI octahedra, and through them the band gap. Kanatzidis and coworkers¹⁴ studied the dependence of the valence band maximum (VBM) and conduction band minimum (CBM) as a function of chemical composition, and concluded that in MASnI3–xBrx the widening of the band gap with the amount of Br is due to an increase in CBM rather than a lowering of VBM. Snaith and coworkers confirmed the findings of Seok and coworkers,⁷ and showed that a correlation exists between \(E_g\) and the pseudocubic lattice parameter of the crystalline sample.⁷ This relation inspired them to use the size of the monovalent cation, A, as...
Cs+ in the cubic CsPbI3 with NH4+ characterized by a tilting angle along all of their three axes (orthorhombic). Tetragonal CsSnI3 is along their axis parallel to the tetragonal axis (tetragonal structure) or been developed in parallel by Gratzel and coworkers, and orthorhombic structures of CsPbI3 are shown, respectively. They also explored the effect of using a mixture of MA and formamidinium (FA) cations. While each of the aforementioned models is valid in the scope of the specific system under study, generalizations and extensions to other compounds are not so straightforward. For example, the conclusions of Amat et al.,12 are somewhat counterintuitive in the light of the results of Snaith and coworkers,10 where it is shown that FASnBr3, which has a cubic structure and smaller lattice constant, has a larger band gap than the tetragonal FASnI3. This apparently conflicting results suggest that there is a significant interplay between changes in the chemical composition and variations of the structure of the perovskite, and the combined effect of these two parameters on the band gap is non-trivial.

The intricacy of the relation between chemical composition (beyond the substitution of monovalent cations), crystal structure and the electronic properties of perovskites calls for a comprehensive theory. Such a theory should aim at rationalizing experimental and computational results in terms of the effect of all essential variables, such as chemical composition, lattice size, as well as distortions in the form of tilting angles, on the electronic structure, and thus on the optical properties of perovskites. This is the objective of the present work. We consider a wide range of perovskites, differing in the chemical nature of the bivalent (Pb and Sn) and monovalent (Na, Li and Cs) cations, halogen composition (I, Br, Cl), and crystal symmetry (cubic, tetragonal and orthorhombic). We also considered lead-iodide perovskites with A = NH4+ versus PH4+ to investigate the specific effects of hydrogen bonding on the electronic structure.

To this end, we performed density functional theory band structure calculations and analyzed the nature of VBM and CBM in terms of atomic orbitals. Interestingly, the character (i.e. the atomic orbital composition) of the band edges (VBM and CBM) remains largely unchanged for this wide range of different chemical and crystallographic variations. This observation suggested the use of an orbital-based parameter as a central descriptor to predict band gap variations. In fact, we show here how the effects of chemical composition and crystal structure on the band gap can all be explained using such a parameter. Finally, as a rule of thumb, we show that strategies for tuning VBM and CBM energy levels, and the band gap must be crystal symmetry-dependent since cubic and tetragonal/orthorhombic structures follow different design guidelines.

2 Results and discussion

2.1 Variations in the crystal structure

We have performed DFT calculations for all chemical compositions (A = Na, Li and Cs, B = Pb and Sn and X = I, Br, Cl) in three perovskite phases. The resulting optimized cell parameters show that the chemical nature of halides and bivalent cations affects mainly the lattice constants (Fig. 1D), as expected on the basis of the well-established empirical relations between the ionic radii and the perovskite lattice size.7 The effect of substituting the monovalent cation, on the other hand, depends on the crystalline symmetry of the reference system. If the system is cubic, the replacement of the original cation results in a corresponding change of the lattice parameter of the crystal: if the new cation is larger, the lattice expands, if it is smaller the lattice constant decreases if it is larger (see Fig. 1G and E). The tilting angle(s), instead, increases if the new cation is larger and decreases if it is smaller (see Fig. 1G and E). This effect of substitution on the lattice size is analogous to the cubic case: larger cations expand the lattice, and vice versa. The tilting angle(s), instead, increases if the new cation is smaller, and decreases if it is larger (see Fig. 1G and E). This affects the linearity of the B–X–B angles: the more the structure is tilted, the more the B–X–B angles depart from the 180° value of the cubic structures. We observed values of θ in the range ~7–19.5° for the non-zero tilting angles in the tetragonal structures, and ~6.5–23° in the orthorhombic ones (where all tilting angles are non-zero). Monovalent cations that form hydrogen bonds with the halides of the framework are a special

![Graphical representation of results and discussion](https://example.com/graph.png)
case. Depending on the strength of the hydrogen bond, the cubic structure may or may not be a (meta)stable form. In fact, the structure obtained by replacing Cs\(^+\) with NH\(_4\)^+ in the cubic CsPbI\(_3\) turns out to be triclinic, with crystallographic angles \(\alpha = 85.8^\circ\) and \(\gamma = 87.1^\circ\). Moreover, strong hydrogen bonds induce deformations of the BX\(_6\) polyhedra (Fig. 1H). If Cs\(^+\) instead is replaced by a weaker hydrogen bond donor cation, e.g. PH\(_4\)^+, a stable cubic structure is obtained (Fig. 1I).

2.2 Variations in the electronic structure

To understand the origin of the experimentally observed band gap variations, we have characterized the influence of the chemical nature of A, B and X, and the crystalline symmetry on the VBM and CBM. It is worth remarking that simple hypotheses to explain the observed phenomenology, e.g. that the energy of VBM and CBM changes because the energy of the corresponding atomic orbitals change with the nature of the halide, turn out to be inadequate. Our calculations show that the difference between the VBM and CBM energy of perovskites formed by different halides change in a range of \(\sim 2\) eV (see Fig. S1†), and sometimes have an opposite sign with respect to the difference of energy between p atomic orbitals of the different halides \(\Delta E_{p\text{Br}} - \Delta E_{p\text{Cl}} = 0.5 - 0.6\) eV. Thus, it is clear that other effects, discussed in the following, are responsible for the high tunability of the valence and conduction band energy, and, thus, the band gap of halide perovskites.

An interesting feature of all perovskites considered in this work is the universality of the electronic characteristics of their VBM and CBM. In fact, in all systems, VBM is formed by an antibonding combination of B ns and X mp orbitals, namely Sn-5s or Pb-6p, and Cl-3p, Br-4p or I-5p (see Fig. 2), also in agreement with previous findings.\(^{18,19}\) This orbital has a high covalent character, with a typical B/X atomic orbital contribution of \(\sim 30-40\%\), depending on the chemical nature of A, B and X, and the crystal symmetry. CBM is also characterized by an antibonding combination, this time by B np and X ms orbitals (see also ref. 20). In contrast to VBM, the character of CBM is more ionic, with B orbitals contributing \(\sim 70\%\). Therefore it seems that an atomic orbital based model could provide a universal framework to describe the band gap variations. In fact concerning the VBM level, the effect of changing symmetry, from cubic to tetragonal to orthorhombic, is reducing the overlap between B ns and X mp orbitals (see Fig. 2A-C). In the cubic structure X mp orbitals are aligned along the B-X bond. This alignment is worse in the other two structures; in particular it decreases along the series cubic \(\rightarrow\) tetragonal \(\rightarrow\) orthorhombic. As for monovalent cation substitution, an effect is observed that depends on the symmetry of the crystal. In cubic systems, in which the size of A affects only the size of the lattice, we observe an increase or decrease of the (negative) B-ns/X-mp overlap with the size of the cation. In tetragonal and orthorhombic crystals, in which the size of A affects both the lattice size and the tilting angles, two competing effects are present: increase or decrease of the B-ns/X-mp overlap due to (i) size of the lattice and (ii) the extent of tilting. The overlap increases with the shrinking of the lattice, like in the case of cubic systems, and decreases with the increase of \(\theta\). Calculations show that, typically, the second effect dominates, and the overlap is reduced in systems with smaller A. The chemical nature of A can affect VBM orbitals also in a more direct way, via polarization. This occurs when A can establish a relative strong bond with the halide of the framework, like for instance hydrogen bonds (Fig. 2D). The effect is twofold in this case. First, because the structure is highly distorted, the alignment of X-mp orbitals with B-X bonds is very poor. Second, the electron density on the X ion hydrogen bonded to A is higher, with corresponding charge depletion on the adjacent B cation and the remaining X ions. Both effects cooperate in reducing the antibonding B-ns/X-mp overlap. Finally, concerning the effects of halide substitution, the change of the chemical nature of this species affects mainly the geometry of the system by shrinking/ expanding the lattice. However, the size of the p orbitals of X do not shrink/expand by the same amount, thus producing a change in the antibonding overlap with the halide composition of the perovskite.
In summary, for what concerns the tunability of the VMB, all
the changes induced by variations in chemical composition and
crystal structure can be rationalized in terms of the overlap
between the B ns and X mp atomic orbitals forming this state.
According to a tight binding formulation, the energy of a crystal
orbital depends on the overlap among the relevant atomic orbitals.
In particular, the larger is the negative (antibonding) overlap
the higher is the energy of the state. This argument, together with
the above analysis, suggests that the key observable correlating
with $E_{\text{CBM}}$ is the orbital overlap; A, B and X substitutions, and the
symmetry are all effective ways to alter the B ns/X mp overlap.
To validate this idea we computed the overall overlap in the
VBM orbital, $O_{\text{VBM}} = \text{Re} \left( \sum_{i} \sum_{j} \hat{c}_{i,j}^{2} / \sqrt{\hat{c}_{i}^{2} \hat{c}_{j}^{2}} \right)$, with

$$O_{ij} = \int dr \phi_{i}(r) \phi_{j}(r)$$

being the overlap between pairs of X and B
atomic orbitals, and $c_{i}$ and $c_{j}$ projection coefficients of crystal
orbitals onto the atomic ones. In Fig. 3, the correlation between
$O_{\text{VBM}}$ and $E_{\text{VBM}}$ is shown. The fitting of this correlation with
a linear function is very good for Sn-based perovskites (regression
coefficient $R^2 \approx 0.93$), while it is somewhat poorer for Pb-based
systems ($R^2 \approx 0.52$). However, for Pb-perovskites of single halides
the correlation is once again linear ($R^2 \approx 0.85$). The VBM energy
of single halide Pb-perovskites follows the order $E_{\text{VBM}}^{\text{Cl}} < E_{\text{VBM}}^{\text{Br}} < E_{\text{VBM}}^{\text{I}}$. This small but nonnegligible effect is due to the energy
variations of X np orbitals, which grows along the series just
introduced. The chemical nature of the halide is more important
in the case of Pb perovskites because the VBM orbital is more ionic
than in corresponding Sn-based systems. We also notice that the
slope of the linear fitting is high in both Sn and Pb-based perovskites,
indicating a high correlation between $O_{\text{VBM}}$ vs. $E_{\text{VBM}}$. This
confirms our analysis, that all the modifications considered in
experiments affect the band gap via the B ms and X np overlap.

The above argument can be also invoked to explain the
dependence of the CBM on chemical composition and crystal
symmetry. Also in this case, $O_{\text{CBM}}$ vs. $E_{\text{CBM}}$ data show the expected
trend of a decrease of the energy of the CBM with the
overlap. However, data are more scattered and the slope is
lower, suggesting a poorer correlation between the two observables.
In the case of the CBM, the change of energy is mainly
due to the electron density transfer from B to X (or vice versa)
induced by the change of chemical composition and crystal
structure (see Fig. 2E and F and 4 and S4†). Since the region
around B is positive, and that around X is negative, moving
charge from B to X increases the electrostatic energy of the
orbital. This explanation is proven to be correct by computing the
correlation between the charge on the B ion, $q_{\text{B}}$, and $E_{\text{CBM}}$.
Indeed, there is a clear linear correlation between these two observables for the various perovskites of given B and X ions.
The effect of changing halides from I to Br to Cl is to shift this
linear correlation to higher energy values. This is because the Cl
environment, which is more negative, is more repulsive to an
additional electron than Br, which, in turn, is more repulsive than I.

It is remarkable that the composition and structural
parameters affecting $q_{\text{B}}$ in the direction of increasing $E_{\text{CBM}}$ affect
$O_{\text{VBM}}$ and $E_{\text{CBM}}$ in the opposite direction (Fig. S5†). Thus,
a single parameter, $O_{\text{VBM}}$, can be used to explain the entire
experimental and computational phenomenology. The consequence
of this fact is twofold. First, that chemical or structural
alterations affect $E_{\text{CBM}}$ by a synergic action on $E_{\text{VBM}}$ and $E_{\text{CBM}}$: they
change simultaneously in the direction of opening or closing
the band gap (Fig. S1†). Second, at variance with other light
harvesting materials, it is therefore not easy to tune the energy
of the valence and conduction band of perovskites indepen-
dently to optimize at the same time light harvesting and charge
injection into the hole and electron transport materials.
However, this does not mean that specific changes cannot affect
more one than the other band. In fact, we found that specific
modifications affect the two bands in different ways. Rather, we
must conclude that for halide perovskites, while it is possible to
derive simple design rules for the variations in the energy gap, it
is not straightforward to derive similar guidelines for the
change in the energy of VBM and CBM.

3 Conclusions

In a search for an unified criteria controlling the band gap of
metal halide perovskites, ABX3, we performed electronic structure
calculations on a vast number of compounds differing in chemical
composition and crystallographic structure. Throughout
these variations the atomic orbital composition of CBM and VBM
remained intact, which suggested the use of orbital-overlap based rationalization scheme. In fact, doing so one can predict the effects of different chemical and structural variations in a simple way. In summary, chemical and structural changes increasing the negative overlap between orbitals of B and X ions result in a shrinking of the band gap. This principle can be used to suggest practical rules for tuning (lowering) of the gap. An increase in overlap can be achieved by choosing B and X so as to reduce the ratio between the lattice constant and the size of their respective s and p orbitals. In practice, it is possible to estimate this ratio by using ionic radii as a proxy for the lattice size,37 and covalent radii as a proxy for the size of B and X orbitals. For example, the variation of \(E_g\) with halide composition follows the trend of the ratio \(\alpha = r_l/r_{cl}\) between their ionic \(r_l\) and covalent \(r_{cl}\) radii: \(\alpha_l = 1.47; \alpha_{Br} = 1.58; \alpha_{Cl} = 1.67\). As for the substitution of the monovalent cation, in the case of tetragonal and orthorhombic structures, A must be large so as to reduce the tilting angles, which makes the structure as cubic-like as possible. At the same time, A should not make strong hydrogen bonds with the perovskite framework. Thus, cations that do not form hydrogen bonds are preferable. For example, \(\text{PH}_4^{+}\) is better than \(\text{NH}_4^{+}\); the former is larger than the latter, and it forms weaker hydrogen bonds.

4 Methods

Density Functional Theory (DFT) calculations are performed using the Quantum Espresso suite of codes.23 We use the Generalized Gradient Approximation (GGA) to density functional theory in the Perdew–Burke–Ernzerhof (PBE) formula22 and, for selected systems, the range separated hybrid exchange and correlation functional of Heyd, Scuseria, and Ernzerhof (HSE).21 The interaction between valence electrons and core electrons and nuclei is described by ultrasoft pseudopotentials. Norm conserving pseudopotentials are used in the case of HSE calculations. In GGA calculations, Kohn–Sham orbitals are expanded in a plane wave basis set with a kinetic energy cutoff of 40 Ry, and a cutoff of 240 Ry for the density in the case of ultrasoft pseudopotentials. HSE calculations are performed with a cutoff of 60 Ry. The Brillouin zone is sampled with a \(3 \times 3 \times 3\) and \(4 \times 4 \times 4\) Monkhorst–Pack \(k\)-points grid24 for cubic and tetragonal/orthorhombic structures, respectively. The above values are chosen by checking the convergence of total energy, band gap and atomic forces.

Sn-Based computational systems are prepared starting from experimental structures for CsSnBr\(_3\),35 replacing Cs\textsuperscript{+} with Na\textsuperscript{+}, Li\textsuperscript{+}, NH\(_4\)\textsuperscript{+} and PH\(_4\)\textsuperscript{+}; and Br\textsuperscript{−} with Cl\textsuperscript{−} and I\textsuperscript{−}, as needed. Structures (atomic positions and lattice parameters) are then fully relaxed. Cubic samples consist of a \(2 \times 2 \times 2\) supercell containing 8 stoichiometric units. For the body-centered tetragonal structures, we considered the simple tetragonal analogue, which contains 4 stoichiometric units. Finally, for the orthorhombic structure we used the experimental unit cell, which already contains 4 stoichiometric units. Pb-Based samples are created using the same protocol starting from experimental structures of ref. 26 and 27.

On the optimized structures, bands calculations are performed including Spin Orbit Coupling effects (SOC) according to the method proposed by Dal Corso and Mosca Conte.28 For this, pseudopotentials obtained from fully relativistic all electrons atomic data are used.

Comparing the energy of Kohn–Sham (KS) orbitals in solid-state systems is difficult because in periodic boundary calculations there is no reference value. Several techniques have been developed to cope with this problem. Two well established techniques are based on the study of interfaces or surfaces (i.e. an interface with vacuum). Which one to adopt depends on the problem at hand, whether one is interested in the interface between two materials or the effect of a surface on the bands. Another technique has been used in the case of both bulk and interface systems. This consists in taking as reference localized deep impurity states29,30 or the atomic states of the chemical species present in the system, e.g. the O-2s states in refs. 31–34, (i.e. states that are expected to be unaffected by the chemical and structural nature of the system). The rational behind this approach is that the energy of these states is not expected to change from one computational sample to another. Thus, any change in their energy observed among a set of systems is due to the arbitrary shift associated to the lack of any absolute reference. The difference of energy of this state among the systems of the set can be used for an alignment of their bands. This procedure is illustrated in Fig. S7.† One drawback of this approach is that it is not general like the interface/surface based alignment procedures, as one has to rely on the existence of such atomic states. Nevertheless, if such states are present, this procedure provides an accurate and computationally cheap approach for defining a proper reference.

In the present case, we use as reference nd orbitals of Pb and Sn. In Fig. S7† the density of states (DOS) of orthorhombic CsPbI\(_3\), LiPbI\(_3\) and CsPbBr\(_3\), and tetragonal CsPbI\(_3\) are shown. It is evident that while the other bands change among the four systems the band at \(\sim 15\) eV, corresponding to Pb-5d is only rigidly shifted, supporting the hypothesis that the vacuum levels of these atomic orbitals are independent of the system considered in the present work. To further confirm the reliability of this approach, we compared the DOS as obtained by the atomic orbital alignment and the well established vacuum level alignment (Fig. S7,† panels B and C). The vacuum level alignment has been obtained on the basis of the electric potential of a 8 unit cell slab model of the perovskites surfaces, shown in Fig. S8.† As can be seen from Fig. S8,† the two alignment procedures are equivalent in the present case, with a maximum difference of \(\sim 0.03\) eV between the two procedures, which is within the accuracy of DFT calculations.

Acknowledgements

We thank Alfredo Pasquarello for fruitful discussions. U. R. acknowledges funding from the Swiss National Science Foundation via individual grant No. 200020-146645, the NCCRs MUST and MARVEL, and support from the Swiss National Computing Center (CSCS), the CADMOS project. We also acknowledge PRACE for awarding us access to resource SuperMUC based in Germany at Leibniz.
References

4 http://www.nrel.gov/ncpv/images/efficiency_chart.jpg/
7 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, Nano Lett., 2013, 13, 1764–1769.