Contributions to Optical Properties and Efficiencies of Methyl-ammonium Lead, Tin and Germanium Iodide Perovskites

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Abstract

Methyl-ammonium lead, tin and germanium iodide perovskites are very interesting compounds for photovoltaics since they present a high absorption capacity of solar radiation. The microscopic contributions to the absorption coefficients and efficiencies of these perovskites are analyzed and quantified. To achieve this goal both, absorption coefficients and efficiencies are split as an exact many-species expansion. The absorption coefficients have been obtained from first principles and have been used later to obtain efficiencies. Furthermore, by using the absorption coefficients instead of the bandgap as the criterion for absorption, the efficiencies have also been quantified as a function of cell thickness. The contributions of inorganic cations are larger than that of organic cation atoms for low energies. As a consequence, as the thickness decreases, the contribution to the efficiency of inorganic cations and iodine increases while those of the organic cation decrease.

Keywords: Perovskites; Optical properties; Photovoltaic; Semiconductors.

1. INTRODUCTION

The usual halide perovskites ABX_3 are very interesting compounds for photovoltaics since they present optical properties that can allow high efficiency in photovoltaic conversion (15-20 %^{1,2}). The best solar cells have been obtained from methyl-ammonium lead iodine $CH_3NH_3PbI_3$ which has a bandgap of 1.55 eV, close to

the optimum one for photovoltaic performance (~ 1.3 eV for a sunlight spectrum with the maximum concentration)³⁻⁵. In this case A is the methyl-ammonium organic cation $\text{MA}^+ = [\text{CH}_3\text{NH}_3]^+$, B is the Pb and $\text{X} = \text{I}$. In general, A is an organic (MA, formamidinium, ...) inorganic (alkali metals) monovalent cation, B a divalent cation (Pb, Sn, Ge ...) and X a halogen anion.

In addition to the excellent optoelectronic properties the halide perovskites have other attractive properties such as low density, flexibility, low cost, tunable bandgap, long carrier recombination lifetimes, high electron/hole mobility, and the possibility of novel device structures and new perovskite materials⁶⁻⁸. These properties explain the rapid progress during the last decade in which the maximum efficiency has been improved from $\sim 3\%$ to $\sim 20\%$.

Despite this rapid development, there are still problems to be solved in order to implant solar cells based on perovskite as the absorbent material. One of these problems is the stability upon prolonged exposure to light, humidity, and high temperature. Other problem with the lead-halide perovskites is the toxicity of lead. It is a serious environmental problem for future development in many countries. Therefore it would be suitable to replace the Pb with other cations to avoid these environmental and toxicity problems.

Alternatives to lead should be metals admitting the divalent oxidation state. *A priori*, from the point of view of the electronic structure, the best alternatives would be the replacement of Pb by elements of the same group in the periodic table such as Sn and Ge with similar outer shell *s*-orbitals. Lead iodine perovskite is more stable than tin iodine perovskite Chen⁻⁹. For this reason the first is the most widely used of the group IVA metals. Sn^{2+} easily transforms into Sn^{4+} that gives rise to a metal-like behavior in the semiconductor which lowers the photovoltaic performance of this perovskite^{9,10}.

Germanium iodine perovskite has been studied less than Pb and Sn perovskites, possibly due to its highly unstable nature in the divalent oxidation state ^{9,10}.

One of the properties that determine the conversion of solar energy is the absorption coefficient. We will use first principles to evaluate them. Furthermore, the absorption coefficients have been split into contributions due to excitations between the atomic species. This split allows the most important contributions to be identified and quantified as a function of the photon energy. Similarly the efficiencies have been split and quantified as a function of cell thickness. This will be described in the methodology section. After that, the results are presented and compared with other theoretical and experimental results. Finally, the main conclusions of this work are set out.

2. METHODOLOGY

In order to obtain the electronic and optical properties, density functional theory (DFT) ^{11,12} calculations were carried out with orbital-dependent one-electron U potentials (DFT+U method ^{13–18}) using the formalism described in references ^{15,16}. For the exchange-correlation potential we use the generalized gradient approximation (GGA) from Perdew, Burke and Ernzerhof ¹⁹, the Troullier–Martins ²⁰ pseudopotentials expressed in the Kleinman–Bylander ^{21,22} form, and a numerically-localized pseudoatomic orbital basis set ²³ for the valence wave functions. Generally the use of a localized basis set combined with the GGA-PBE functional provides reasonable estimates of the bandgaps in organic-inorganic metal halide perovskites ²⁴. It represents a compromise between accuracy and computational cost.

In all results presented we use periodic boundary conditions, double-zeta with polarization localized basis sets, and 256 k-point grids to sample the Brillouin zone. The parameters of the structures used in the calculation were taken from reference ²⁵:

$(a|b|c|\alpha|\beta|\gamma) = (6.459 \text{ \AA} | 6.441 \text{ \AA} | 6.525 \text{ \AA} | 87.42^\circ | 86.79^\circ | 92.85^\circ)$ for M=Pb, $(6.395 \text{ \AA} | 6.378 \text{ \AA} | 6.489 \text{ \AA} | 86.79^\circ | 85.88^\circ | 92.30^\circ)$ for M=Sn, and $(6.338 \text{ \AA} | 6.160 \text{ \AA} | 6.199 \text{ \AA} | 91.06^\circ | 94.82^\circ | 88.08^\circ)$ for M=Ge.

The optical properties were obtained from the complex dielectric function using the Kramers-Kronig relationships²⁶. They can be expressed as an exact many-species expansion^{27,28} with terms that involve up to 4 species. It allows the different contributions to the absorption coefficient $\alpha = A_{12} + A_{34}$ to be evaluated. The first term involves intra-species (A=B) and inter-species (A≠B) contributions $A_{12} = \sum_A \sum_B \alpha_{AB}$, and A_{34} involves 3-species (A≠B≠C) and 4-species (A≠B≠C≠D) contributions. In binary compounds there is no term of three or four species ($A_{34}=0$ and $\alpha \approx A_{12}$). For the $\text{CH}_3\text{NH}_3\text{MI}_3$ (M=Pb, Sn, Ge) perovskites with 5 different species (C, H, N, M, I), the number of A_{12} and A_{34} terms is 10 and 20 respectively. The number of A_{34} terms increases rapidly with the number of species of the compound, and therefore its contribution to the absorption coefficient.

In a photovoltaic converter, assuming that each absorbed photon creates an electron-hole pair (quantum efficiency=1), the current generated by the photon absorption from an incident spectrum g_a is³⁻⁵: $J_a = q \int a(E, \alpha, w) g_a(E) dE$. In this expression $a(E, \alpha, w) \approx 1 - e^{-\alpha w}$ is the absorptivity, α the absorption coefficient, w the optical thickness, and q is the electron charge. In this work we have used the AM1.5G²⁹ spectrum for g_a . The absorption process is always accompanied by an emission process because of the radiative recombination with an emission current $J_e = q \int a(E, \alpha, w) g_e(E) dE$, where g_e is the photon flux density emitted. It is usual to consider that the solar cell emits radiation as a generalized Black-body at a temperature

$T=300\text{ K}$ ³⁻⁵. In this case $g_e(E) \sim E^2 b(E, T, qV)$, where $b(E, T, \mu) = [e^{(E-\mu)/kT} - 1]^{-1}$ is the Bose factor, k the Boltzmann constant, V the voltage, and $\mu = qV$ the chemical potential associated with the radiation emitted ³⁻⁵. Then the useful current is $J(V) = J_a - J_e(V)$, and the efficiency $\eta = JV / P_{inc}$ where P_{inc} is the irradiance of the incident sun-light spectrum.

If the absorption coefficient is split as a many-specie expansion ^{27,28}, i.e. as a sum of $\alpha = \sum_B \alpha_B$, different α_B compete for the same photons. In this case the current associated to the absorption coefficient α_B is $J_{\kappa}^{(B)} = q \int a \cdot (\alpha_B / \alpha) \cdot g_{\kappa} dE$ ($\kappa=a$ and e for the absorption and emission processes respectively). Then the total current and efficiency are $J = \sum_B J_B$ and $\eta = \sum_B \eta_B$, where the contribution to the efficiency η from α_B is $\eta_B = J_B V / P_{inc}$. This efficiency splitting is also exact because the splitting of the absorption coefficient as a many-species expansion is exact.

3. RESULTS AND DISCUSSION

The experimental bandgap reported in the literature for MAMI_3 with $\text{M}=\text{Pb}$, Sn and Ge are between 1.55-1.61 eV ^{30,31}, 1.2-1.4 eV ^{30,32,33}, and 1.90 eV ³² respectively. The bandgaps obtained theoretically are 1.23-1.85 eV ^{24,34-38}, 0.59-0.61 eV ^{34,39}, and 1.17 eV ³² for $\text{M}=\text{Pb}$, Sn , and Ge respectively. For $\text{M}=\text{Pb}$ these calculated bandgaps are in general in good agreement with reported experimental values.

The bandgaps obtained in this work with DFT-GGA are 1.60 eV, 0.60 eV and 1.0 eV for $\text{X}=\text{Pb}$, Sn and Ge respectively. Thus, while for $\text{M}=\text{Pb}$ the experimental bandgap is reasonably reproduced, for the $\text{M}=\text{Sn}$ and Ge the bandgaps are underestimated. In order to avoid the DFT-GGA bandgap underestimation problem and avoid using a scissor operator to describe the bandgaps correctly we have used the DFT-GGA+U

scheme described in the methodology section. Note that the DFT-GGA+U calculations are not equivalent to DFT+GGA with the application of a scissor operator. The former are self-consistent calculations. Therefore it is more reasonable physically than applying a scissor operator to the DFT-GGA results. In this way, the theoretical gap will be more similar to the experimental values, but considering the orbital interactions self-consistently. The U parameter has been set to zero for M=Pb and U = 5 eV for the M=Sn and Ge. The gaps obtained are in accordance with the experimental bandgaps (1.6 eV, 1.3 eV and 1.9 eV for M=Pb, Sn and Ge respectively).

In all cases the electronic structure has similar characteristics: the valence band (VB) top is made up predominantly of the p(I) orbitals, and the bottom of the conduction band (CB) is mainly of a p(M) character with a smaller contribution from the p(I) orbitals. It is in agreement with other references in the literature^{32,34,34,35,40}.

The sunlight absorption properties are determined by the absorption coefficient. The absorption coefficient reflects the combination of the overall structural, electronic and optical properties of the material. But it does not give us any information on the main contributions of the species or the orbitals. This information would be very useful to analyze the main contributions and to relate the absorption coefficient with the composition and the structure of the materials. To achieve this goal the absorption coefficients have been split into many-species expansion as described in the methodology section.

The efficiencies for the transformation into useful work from the absorbed solar radiation depend on the absorption coefficients. Therefore, the splitting of the absorption coefficients also allows the efficiencies to be split. According to the procedure described in the methodology section, both absorption coefficients and efficiencies have been broken down into contributions between species. The most

important inter- and intra-atomic contributions, as well as the total contribution of the terms of one and two species (A_{12}), and those of 3 and 4 species (A_{34}) are shown in Figure 1 for the absorption coefficients, in Figure 2 for the efficiencies using the AM1.5G spectra ²⁹, and the percentage contribution of the split species contributions efficiencies with respect to the total efficiency in Figure 3.

The results in Figure 1a for M=Pb is in accordance with the experimental results in the literature: presence of absorption bands between 2.5-2.7 eV ⁴¹ attributed to inter-species Pb-Pb ⁴², and between 3.2-3.5 eV ⁴¹ from the I-I, Pb-I and Pb-Pb species transition in descending order of importance. These experimental absorption bands are represented with shaded areas in the figure. Furthermore, the absorption coefficient for M=Pb reproduces the drop of the experimental absorption band of between 3.5 and 4 eV ⁴¹.

The experimental spectrum of the Sn-based perovskite ³³ has a small peak at ~1.8 eV and a wide peak centered at ~2.2 eV (vertical lines in the Figure 1b). These peaks can be compared with the absorption coefficient peaks in Figure 1b at 1.7 eV and 2.1 eV because of the Sn-Sn inter- and intra-atomic excitations.

Furthermore, the results in Figure 1c for M=Ge indicate three absorption peaks around 2.15 eV, 2.3 eV, and 2.7 eV mainly due to the Ge-Ge contributions. These peaks compare reasonably well with the experimental absorption peaks around 2.15 eV, 2.25 eV and 2.62 eV ⁴³ (vertical lines in the figure).

The absorption coefficients (Figure 1) are on average lower, for photon energies within the energy range shown in the figures, for Sn and Ge than for Pb. Nevertheless the Sn-based perovskite has greater efficiency (Figure 2) because Sn has a smaller and closer to optimum bandgap to obtain maximum efficiency (~1.1-1.3 eV for a sunlight spectrum with the maximum concentration and without solar spectrum concentration) ³⁻

⁵. The contribution of A_{12} and A_{34} species terms to the efficiency are similar for optical thicknesses $w \leq 1 \mu\text{m}$ (Figures 2 and 3). However, for smaller w the contribution of A_{12} increases while that of A_{34} decreases. This is because the term A_{34} has a large contribution to the absorption coefficient, similar to A_{12} , but for higher energies.

The energy to which an optical transition between two states contributes to the absorption coefficient is the energy difference between the initial and final states. The main contribution of the A_{12} terms corresponds to transitions between M-M, M-I and M-I states (Figure 1). As previously mentioned these states contribute mainly to band edge perovskite states. Therefore its contribution to the absorption coefficient will be high for energies close to the bandgap. The states corresponding to the organic cation atoms contribute almost nothing to the band edge perovskite states. Their contribution is for energies farther from the edges of the VB and CB, i.e. deeper into the VB and CB. Therefore, the energy difference between these states, which contributes mainly to the A_{34} term, is larger than that of the states that contribute to the A_{12} term. As a consequence, the A_{34} term will contribute to the absorption coefficient for larger energies (farther from the bandgap) than the A_{12} terms (closer to bandgap) as the results show in Figure 1. Then, so that the contribution of A_{34} to the efficiency to be large the thickness of the cell must also be large. If the thickness of the cell is small, the higher energy photons (where A_{34} contributes more than A_{12} to the absorption coefficient) are not absorbed by the solar cell and do not contribute to the efficiency. In accordance with the results in Figure 2, the M=Sn perovskite has the greatest potential for solar cells considering only the absorption capacity. However it is not used because it

degrades easily as a result of Sn^{2+} oxidation to Sn^{4+} upon contact with air producing SnI_4 .⁹

As has already been mentioned the calculations with DFT-GGA+U are not equivalent to the application of a scissor operator to the DFT-GGA results (i.e. with $U=0$). The application of the scissor operator modifies the properties only by displacing the bandgap, but without modifying the relative interactions between states. However, with DFT-GGA+U both the bandgap and the orbital interactions are self-consistently modified. Obviously it has consequences on the efficiencies.

In Figure 4 the absorption coefficients with DFT-GGA ($U=0$) and DFT-GGA+U ($U=5$ eV) are compared for the Sn perovskite. In this figure we have chosen the origin of energies equal to the semiconductor bandgap (0.60 eV and 1.3 eV for $U=0$ and $U=5$ eV respectively). When the semiconductor bandgap is taken as the origin of the energy, i.e. $E-E_g$ is represented on the energy axis instead of E , both theoretically calculated with $U = 0$ and $U = 5$ eV compare reasonably well with experimental absorption peaks³³ (vertical lines in the figure).

The main differences in the absorption coefficients (in mean value) when U increases are a slight increase in the Sn-Sn contribution, a decrease in the I-I contribution and, in a lower proportion, of the Sn-I. This is also reflected in the contribution to the efficiency of the different absorption coefficients (Figure 5). In this figure the efficiency percentages are compared with respect to the total efficiency ($\eta_{split}/\eta_{Total} \times 100$) using the scissor operator with $U=0$ (DFT-GGA) and with DFT-GGA+U ($U=5$ eV). To compare the efficiencies the bandgap with $U=0$ eV is displaced to match the experimental bandgap, equal to that obtained with DFT-GGA+U (1.3 eV). In this figure it can also be observed that the contribution of the A_{12} and A_{34} terms begins to be different (A_{12} increases and A_{34} decreases) for smaller w when U increases.

This is mainly due to the increase (in average value) with U of the differences between the energies of the initial and final states of the optical transitions.

4. CONCLUSIONS

The optical and photovoltaic properties of Methyl-ammonium lead, tin and germanium iodide perovskite are obtained from first principles based on the DFT-GGA+ U . The results are in accordance with the experimental results in the literature.

The absorption coefficient does not provide information on which atomic species contributes most to the optical properties. In order to identify and quantify these contributions the absorption coefficients have been split into an exact many-species expansion. For energies close to the bandgap the A_{12} term contributions are the largest (M-M, and with a lower proportion of I-I, and M-I). The contribution of the organic cation atoms (C, H, N) is mainly to the A_{34} term, similar in magnitude to the A_{12} term but for higher energies.

From the absorption coefficients split as an exact many-species expansion the efficiencies have been obtained and split in a similar way. As a consequence the M-M, M-I and I-I contribute more to the absorption coefficient, and the contribution of these excitations to efficiency is also larger. In all cases (Pb, Sn and Ge), as the A_{34} term contributes to the absorption coefficient for greater energies than the A_{12} term, the A_{34} term reduces its contribution to efficiency when the solar cell absorbing thickness is less than $3\text{ }\mu\text{m}$ ($\log w \sim 0.5$).

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Notes

The authors declare no competing financial interest.

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Figure 1: (left y axis): absorption coefficient split into species contributions of the different MA-M-I₃ structures: (a) M=Pb, (b) M=Sn, and (c) M=Ge. The total absorption coefficient is represented in the right y axis. The shaded region in panel a, and the vertical lines in panels c and d correspond to experimental results in the literature^{33,41,43}.

Figure 2: Efficiency η (%) split into species contributions as a function of the cell thickness w decimal logarithm using the AM1.5G spectra for different MA-M-I₃ compounds: (a) M=Pb, (b) M=Sn, and (c) M=Ge.

Figure 3: Percentage contribution of the split species contribution efficiencies with respect to the total efficiency ($\eta_{split}/\eta_{Total}) \times 100$) as a function of the cell thickness w decimal logarithm using the AM1.5G spectra for different MA-M-I₃ compounds: (a) M=Pb, (b) M=Sn, and (c) M=Ge.

Figure 4: Absorption coefficient split into species contributions for the methylammonium tin iodide perovskite with: (a) GGA ($U=0$) and (b) GGA+ U ($U=5$ eV). The energy origin has been scaled to the energy bandgap. The total absorption coefficient is represented in the right y axis. The vertical lines in panels c and d correspond to experimental results in the literature³³.

Figure 5: Percentage contribution of the split species contributions efficiencies with respect to the total efficiency ($\eta_{split}/\eta_{Total}) \times 100$) as a function of the cell thickness w decimal logarithm using the AM1.5G spectra for M=Sn with $U=0$ eV (thin lines) and $U=5$ eV (thick lines). For DFT-GGA ($U=0$) has been used the same DFT-GGA+ U ($U=5$ eV) bandgap (1.3 eV).