Tight-binding model for mixed perovskites

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***Abstract*—We present a tight-binding description of mixed perovskites showing an application to Sn-Pb mixed systems. We discuss the parameterization procedure and the preliminary results obtained for $MASn_{0.5}Pb_{0.5}I_3$. Our model shows a treatment of the band gap bowing observed for this perovskite alloy when Sn segregation is considered. Note that our method can be easily extended to include the description of all the perovskite crystal phases and more refined strain effects.**

***Index Terms*—tight-binding, perovskites, Sn-Pb mix, segregation**

I. Introduction

Perovskite semiconductors have represented a breakthrough for photovoltaic applications and are gaining increasing attention in the field of optoelectronic devices, due to the combination of suitable and tunable electronic properties with scalable and cost-effective production techniques. While perovskite-based light-emitting diodes, sensors, and detectors are being developed, the optimization of perovskite materials is now crucial to push the efficiency and stability of perovskite solar cells. Multiscale numerical approaches that embed atomic-scale information in device simulations are paramount in this context to design, understand, and predict how the device performance is affected by the microscopic features. In multiscale frameworks, the tight-binding (TB) model has emerged as the best trade-off between computational burden and accuracy. TB is ideal for large systems where *ab-initio* methods become unfeasible, but, as an empirical method, high-quality sets of parameters are vital for the TB model. One typical example is the transferability of parameters sets from pure materials to mixed materials, or alloys.

Here, we propose a TB parameterization procedure to describe mixed perovskites. We show the application to $MASn_xPb_{1-x}I_3$ for a sp^3 TB implementation based on Jancu scheme [1]. Note, however, that the presented approach is a reduced version of a more complex procedure developed in our group [2], easily extendable to a wide class of semiconductors, $sp^3d^5s^*$ basis set, or advanced TB schemes such as the one of Tan et al. [3].

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II. Computational Approach

The onsite and coupling integrals of the TB Hamiltonian are treated as fitting parameters to reproduce target band structures obtained by density functional theory (DFT) calculations [4] at the PBE0 level of approximation, including spin orbit coupling (SOC). We employ a genetic algorithm for the fitting procedure [2]. In the first step, onsite energies and coupling integrals are optimized to reproduce the DFT band structures of unstrained pure materials. We impose that onsite energies and SOC parameters of I atoms are the same for both $MASnI_3$ and $MAPbI_3$ perovskites. The initial guess for the optimization is taken from Boyer-Richard et al. [1]. Then, the band structures of hydrostatically strained samples of pure materials are fitted to determine the TB Harrison scaling parameters. In Fig. 1, we show the results obtained, e.g., for $MASnI_3$. Note that an advanced multi-objective optimization, that fits both the band structures and the wavefunctions characters, is possible following the extended version of the procedure [2].

Finally, the band offset between pure materials is derived from DFT analysis following the method of Weston et al. [5]. This involves two bulk calculations, giving the position of the valence band edge with respect to the average electrostatic potential, and a supercell calculation to determine the electrostatic potential alignment between different materials.

III. Preliminary Results and Future Work

Using the TB implementation available in TiberCAD [6], we tested our TB parameters simulating uniform and Sn-segregated $MASn_{0.5}Pb_{0.5}I_3$ random alloys, for several supercell size values, where the Sn segregation is obtained following the convention in [7], [8] with only 1% of uniformity. When segregation is included, localization of carriers is expected, as shown in Fig. 2, where the spatial distributions of the electron and hole ground-state wavefunctions are represented along with the band alignment between $MASnI_3$ and $MAPbI_3$.

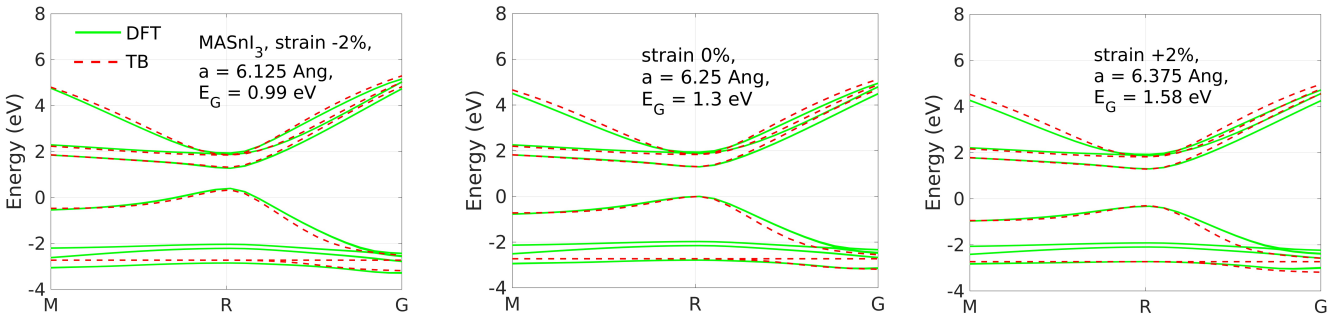

Fig. 1. The band structures of $MASnI_3$ for different hydrostatic strain values reproduced by our TB parameters (red dashed lines) and by PBE0-DFT (green solid lines).

Moreover, the band gap is expected to decrease due to localized states [7], [8]. This effect is shown in Fig. 3, where we report the value of energy gap (E_G) obtained for all the simulated structures. Of course, the size of the supercell becomes important if segregation is considered, since the non-uniform atomic structures produce more scattered results that need statistical significance, highlighting the importance of models capable of handling large systems.

Even if alloy disorder is considered an important factor that strongly affects the electronic properties of semiconductor alloys, other studies [9], [10] demonstrate that the bowing of E_G in Sn-Pb perovskites can be induced by the interplay between SOC and steric effects. As mentioned before, our model includes SOC, but it does not account for structural relaxation, distortion, or even phase transition that is required to reproduce the behavior in [10]. This point will be the focus of our future work. In fact, our parameterization is now restricted to the pseudo-cubic perovskite, but it can be easily extended to the other perovskite phases using the Tan TB scheme [3] and our general parameterization procedure [2]. Moreover, based on molecular dynamics, or even machine-learned force fields, a treatment of structural relaxation could be added.

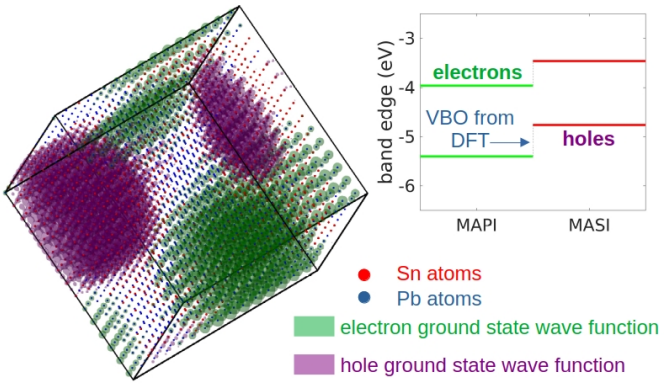

Fig. 2. Spatial distributions of the electron and hole ground-state wavefunctions (isosurfaces containing 50% of the total density are represented) where the presence of Sn segregation is considered. Electrons and holes are localized on Pb and Sn rich regions, respectively, as expected from the band alignment derived by DFT calculations.

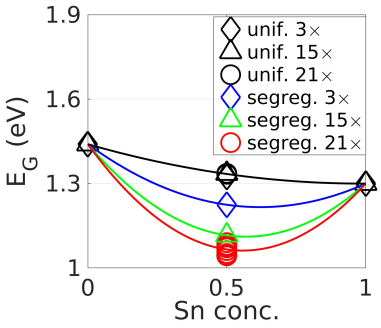

Fig. 3. Trend of E_G as a function of Sn concentration. Several supercell size values are considered for both uniform and segregated structures.

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