

Electronic Supplementary Information (ESI)

Electronic and Geometrical Parametrization of Organic/ Inorganic Cation Role on Photovoltaic Perovskite Band Gap

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PDOS

PDOS for CsPbI₃, MAPbI₃, FAPbI₃ and also their PbI₃ scaffold in the form of top-down are depicted in Figure 1 in range of -10 to +5 eV. Fermi level is shifted to adapt VBM at zero. Contribution of lead and iodine in total DOS are represented in their orbital details as provided in their pseudopotential, i.e. *s*, *p*, and *d* for lead, and *s* and *p* for iodine. The coloring combination was chosen uniformly in all figures. VBM is mainly contributed by 5*p* orbital of iodine, while 6*s* orbital of lead is responsible for CBM (Wang, Xiao, and Wang 2020)(Zhu and Liu 2016). In the case of CsPbI₃, the states of cation (Cs) is 6 eV far from VBM, while a 4 eV of energy level difference could be seen for MAPbI₃ and FAPbI₃. This reveals the more impact of cation in MAPbI₃/FAPbI₃ rather than CsPbI₃. By eliminating cation from the middle of PbI₃ scaffold, while preserving cell parameters and Pb/I positions, the amplitude of total DOS in VBM is increased; Moreover, the band gap is decreased, which is attributed to the impact of cation. Band structure calculation is also confirming the sensible impact of cation on VB rather than CB.

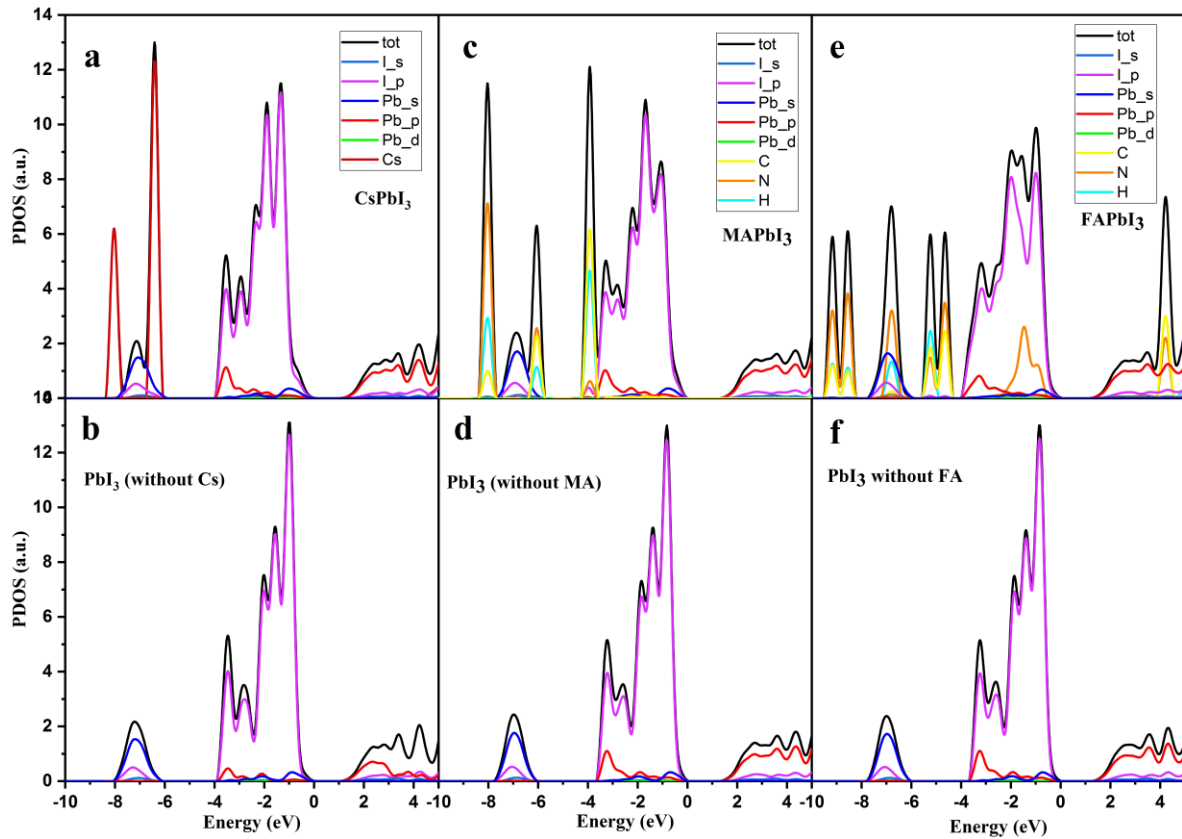


Figure 1: PDOS for (a): CsPbI₃, (c): MAPbI₃, and (e): FAPbI₃ using DFT-1/2. PDOS without the corresponding A-cation (b, d, and f) is also plotted for comparison.

Band structures

Band structure of CsPbI₃, MAPbI₃, and FAPbI₃ using DFT-1/2 method are shown in Figure 2 to Figure 4. SOC is included in all calculations. VBM is adapted to zero. VBM and CBM characteristics are not affected after eliminating cation (red lines). Band gap is slightly decreased. Rashba band splitting due to the spin-orbit coupling of Pb is obvious for MAPbI₃ and FAPbI₃ (Mosconi, Etienne, and De Angelis 2017). Since CsPbI₃ has the perfect cubic symmetry, no splitting is predicted and there is a degeneracy at valence and conduction band. Any band in blue that has not a correspondence red line belongs to cation.

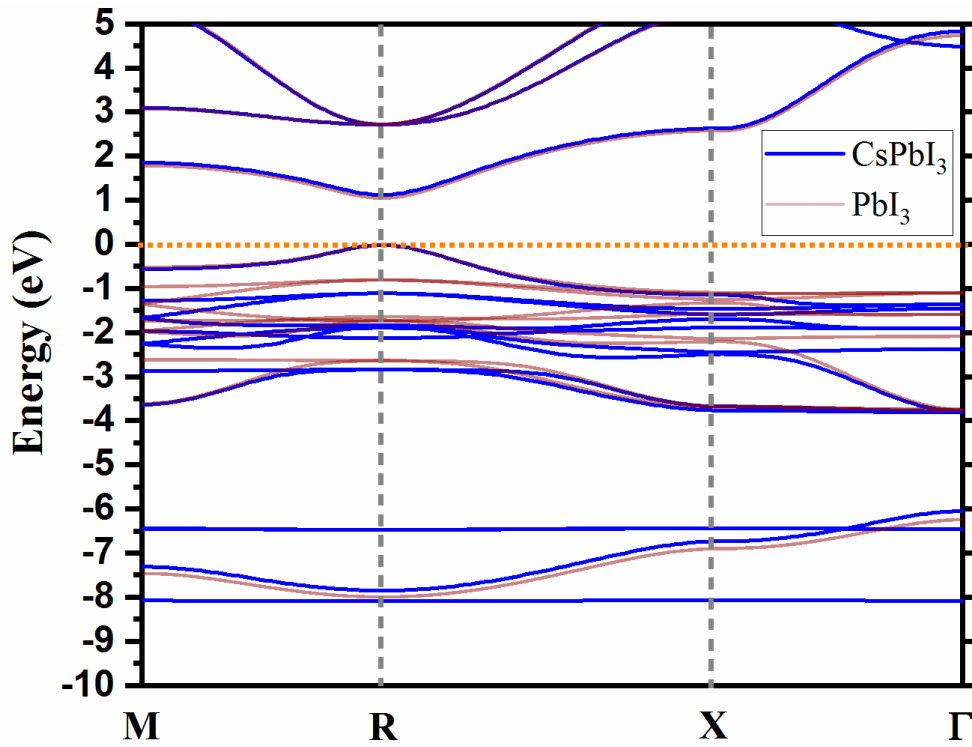


Figure 2: Band structure of CsPbI₃ in blue and PbI₃ (no cation) in red using DFT-1/2 method. Direct band gap is obtained at R point. VBM is adapted to zero.

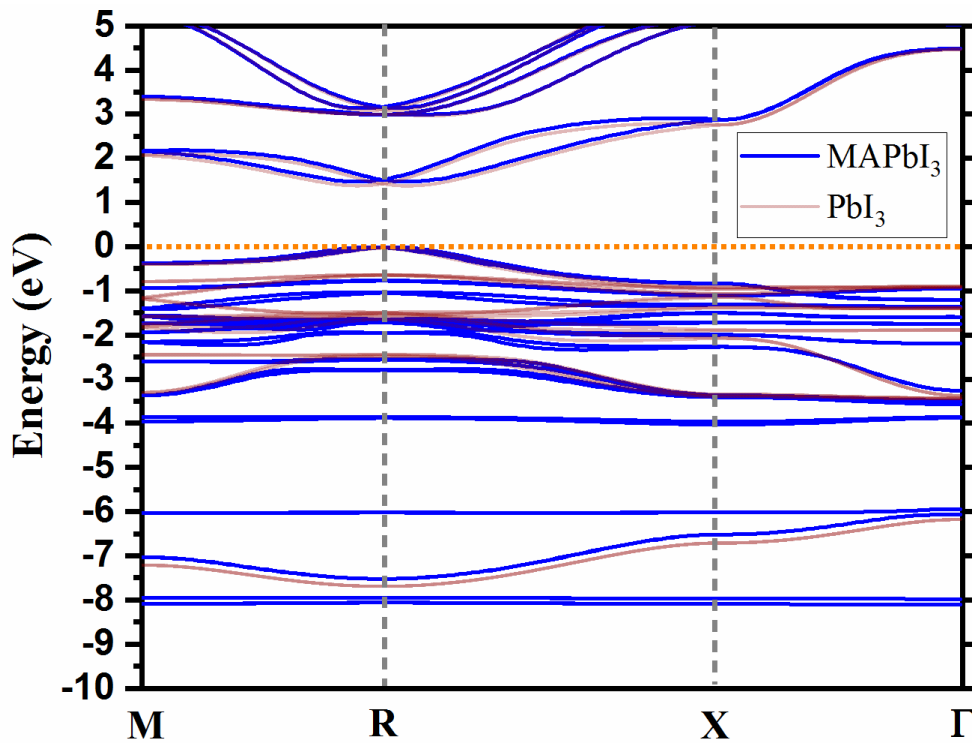


Figure 3: Band structure of MAPbI₃ in blue and PbI₃ (no cation) in red using DFT-1/2 method. Direct band gap is obtained at R point. VBM is adapted to zero.

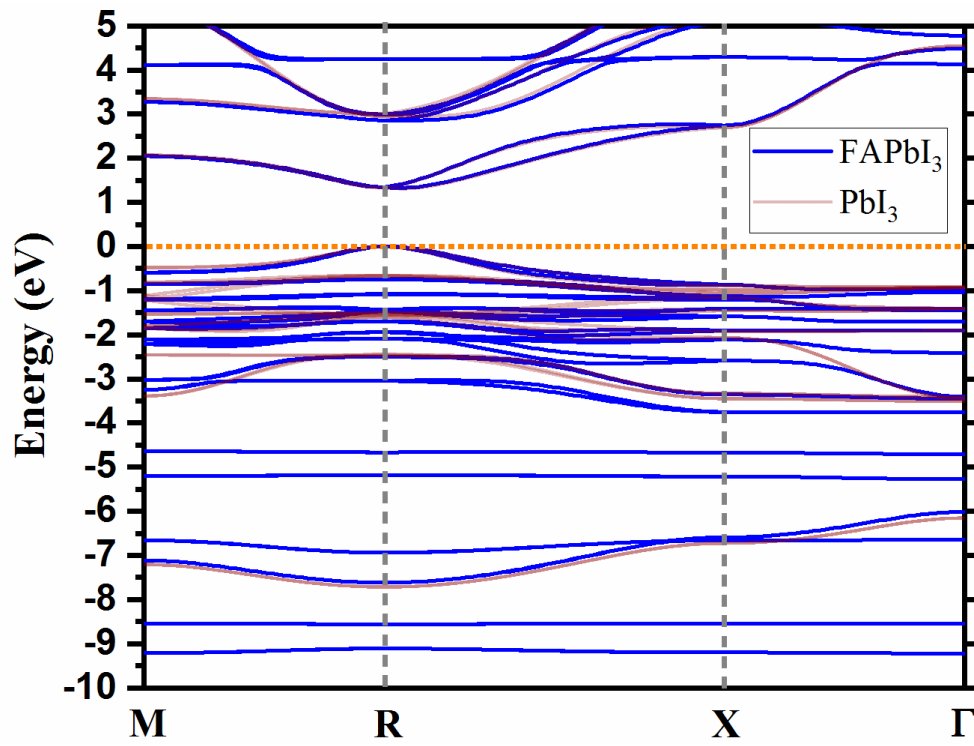


Figure 4: Band structure of FAPbI₃ in blue and PbI₃ (no cation) in red using DFT-1/2 method. Direct band gap is obtained at R point. VBM is adapted to zero.

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- Zhu, H. X., and J.-M. Liu. 2016. "Electronic Structure of Organometal Halide Perovskite CH₃NH₃BiI₃ and Optical Absorption Extending to Infrared Region." *Scientific Reports* 6(1): 37425. <http://www.nature.com/articles/srep37425>.