Supporting Information

"Discovering Lead-Free Perovskite Solar Materials with Split-Anion Approach"

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Optimization of the structures of organic-inorganic hybrid perovskites.

At room temperature, the $CH_3NH_4^+$ cations rotate nearly freely in the voids (i.e., the *A*-sites of perovskite structure) formed by the inorganic framework. The atomic structure and symmetry as measured by experiment are both statistical average. Thus, when modeling these materials, there is uncertainty in the atomic structure adopted in the study. We have considered this effect in our study.

To build the structure of $CH_3NH_3BiSeI_2$, we followed the steps below:

1) Start from the structure of $CH_3NH_3PbI_3$ and replace Pb with Bi and one third of I by Se (see Fig. 1 in the main text). Here we use a 2×2×2 supercell (a = 12.52 Å and b = 12.66 Å) containing 8 formula units (f.u.) of $CH_3NH_3PbI_3$ or $CH_3NH_3BiSeI_2$.
2) Perform variable-cell relaxation (i.e., ISIF = 3 for the VASP code) to optimize both the lattice constants and internal parameters.
3) Using the relaxed structures from step 2), perform *ab initio* molecular dynamics (AIMD) simulation for 13 ps. In the first 3 ps, the system is heated up from 0 K to 300 K. In the next 10 ps, the temperature is maintained at 300 K. Here, we use *NVT* ensemble in the simulation by fixing the lattice constants. A time step of 0.25 fs is used in the simulation.
4) Within the last 10 ps simulation at 300 K, take one snapshot at the end of every 1 ps and then perform variable-cell relaxations on the 10 snapshots.

We found that the variation in the optimized volume, total energy and band gap among the ten relaxed structures are less than 1% of the average volume, 0.05 eV per f.u., and 0.1 eV, respectively.

Because of the random orientation of the $CH_3NH_3^+$ cations, the relaxed structures are not exactly orthorhombic (i.e., with α, β, and γ not 90°). By forcing $\alpha = \beta = \gamma = 90^o$ and $a = b$, we can obtain a tetragonal structure. This tetragonal structure has a slightly higher energy by less than 5 meV per f.u. and a smaller band gap by 0.03 eV. Our analysis of band structure, density of states and the optical absorption was done with this tetragonal structure using PBE functional, while accurate band gap calculations using the HSE+SOC calculation were done with the lowest energy structure from the 10 snapshots.

GW calculation on $CsSnSCl_2$.

The quasiparticle energies of $CsSnSCl_2$ were calculated within the G^0W^0 approximation using a revised version of the BerkeleyGW package with improved performance [1]. The convergence of the G^0W^0 calculation was thoroughly tested. The convergence test is very important for new materials since different materials might have very different convergence behavior [2] of the calculated GW quasiparticle band gap. In addition, the number of bands required for a given level of convergence scales linear with the system size (number of atoms). We included up to 20000 bands (or 1000 bands per atom for a 20-atom unit cell) in both the dielectric function and self-energy calculations. The Hybertsen-Louie Generalized plasmon-pole (HL-GPP) model [3] is used. Interestingly, unlike a related system we investigated earlier [4], the quasiparticle band gap of $CsSnSCl_2$ converges rather quickly with respect to the number of empty states included in the calculation (shown in Fig. S1). The calculate band gap converges to within 10 meV with about 10000 bands (or 500 bands per atom).

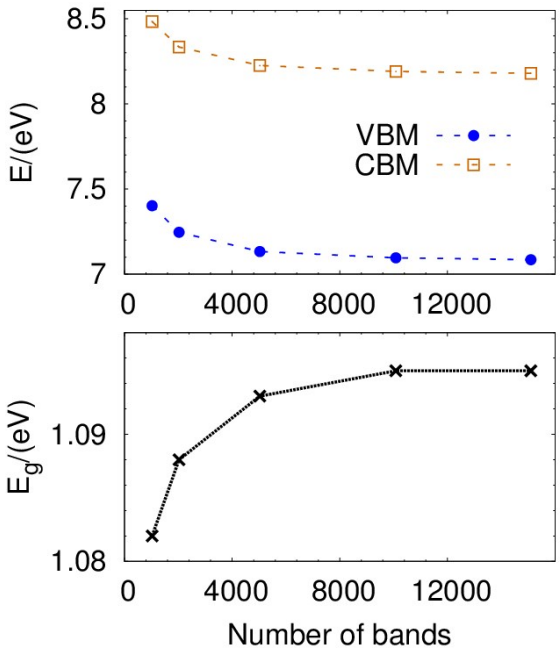

Fig. S1. Convergence behavior of the calculated VBM, CBM energies and the quasiparticle band gap of $CsSnSCl_2$ with respect to the number of bands included in the Coulomb-hole summation.

References:

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