

Electronic structure and phonons in halide perovskites, CsSnX_3 , with $X = \text{Cl, Br, I}$.

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The halide perovskites with formula CsSnX_3 , with $X = \text{Cl, Br, I}$ form an interesting family of materials. The structure consists of corner sharing SnI_6 octahedra which can be viewed as SnI_3^- ions, with divalent Sn, counterbalanced by large positive ions such as Cs^+ . Like other perovskites they have various phase transitions to lower symmetry structures. Using quasi-particle self-consistent GW calculations, and orbital analysis of the bands, we show that their band structures are in some sense inverted and controlled by the intra-octahedron bonding. Unlike most semiconductors which have an s -like conduction band minimum (CBM) and p -like valence band maximum (VBM), these materials have a largely Sn- p like CBM and a VBM which is a mixture of Sn- s and halogen p -states. This circumstance explains a number of the curious properties of these materials, such as an increasing gap with increasing lattice constant and temperature, a strong optical absorption and luminescence, a small hole mass and hence high hole mobility and a gap which is relatively insensitive to the halogen chosen, and the relatively small gaps in spite of the strongly ionic bonding. The band gap of order 1.3 eV in CsSnI_3 and large hole mobility make this material attractive for solar energy conversion.

Next, we are trying to understand the exciton binding energy in this material. Using the effective mass theory of Baldereschi and Lipari we can estimate the binding energy of the exciton in terms of the effective masses extracted from the QSGW band structures. However, an important question now is which dielectric screening to apply to the electron-hole Coulomb interaction. The exciton binding energy estimated using only electronic screening is of the same order of magnitude or slightly higher than the highest phonon frequencies. We calculated the phonon frequencies using density functional perturbation theory. These calculations indicate a ratio of the static dielectric constant to the high frequency dielectric constant of order 4. Using the static dielectric constant including the phonon contributions, the exciton binding energy would be significantly smaller than the experimental value, extracted from the temperature dependence of the photoluminescence intensity.