Elucidating Methylamonium and Cesium based Hybrid Perovskites' Dielectric Properties using Ab Initio Calculations and Ellipsometry Measurements

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Methylamonium lead halide perovskite materials have emerged over the past five years as absorber layers for new high efficiency yet low cost solar cells that combine the advantages of organic and inorganic semiconductors. Similar to inorganic semiconductors, hybrid perovskites (mostly $CH_3NH_3PbI_3$ and more recently cesium-based) have shown low exciton binding energies[1] (≈ 5-30 meV) indicating a potentially high value (≈ 70) at low frequencies for their relative dielectric constant. Others studies have even found giant values (≈ 1000 in the dark) for the dielectric constant[2] at very low frequencies (<1 Hz). Understanding the excitons' physics in these materials is crucial in order to increase the charge extraction and improve the solar cells' efficiency.

Here, we study the phonon modes and dielectric properties of both methylamonium ($CH_3NH_3PbI_3$) and cesium ($CsPbI_3$) lead iodide perovskite structures using DFT (Density Functional Theory) calculations. Phonon frequencies for both the cubic (T>600K) and orthorhombic (T<530K) phases of CsPbI3 are derived using the linear response approach (DFPT). As for the orthorhombic phase (figure 1), we find that $CsPbI_3$ shows a very flat energy profile around its equilibrium structure (figure 2). We derive the dielectric matrix in the high frequency regime (> 1 THz) from the linear response and aim to extract the low frequency dielectric constant from the phonon frequency splitting between normal and longitudinal modes. The results are expected to determine the possibility of a giant dielectric constant for these hybrid perovskites. The dielectric properties obtained for $CH_3NH_3PbI_3$ are being compared to ellipsometry measurements performed in collaboration with Horiba Jobin Yvon company.

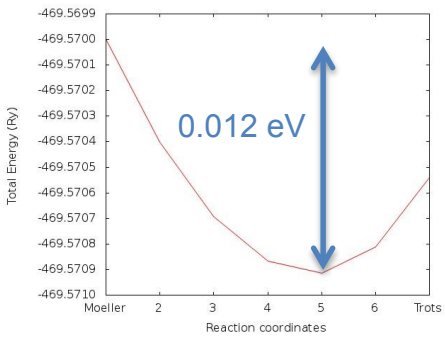

Figure 1: Equilibrium energy of $CsPbI_3$'s orthorhombic phase (T<530K) for 7 sets of atomic positions obtained by DFT. The 5 intermediate position sets are linearly interpolated between sets 1 (*Moeller*) and 7 (*Trots*) which are equilibrium positions relaxed from experimental data[3,4]. The very flat profile indicates potentially low values for acoustic phonon modes.

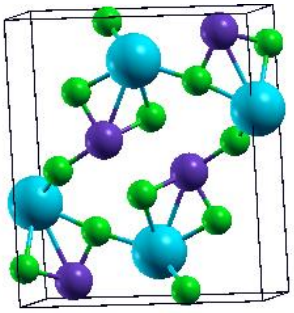

Figure 2: Equilibrium structure of $CsPbI_3$ in its orthorhombic phase for position set 5. The atomic positions are relaxed, and the blue, purple and green atoms respectively denote Cs, Pb and I.

References

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