Elucidating the Dielectric Properties of Methylamonium and Cesium based Hybrid Perovskites using *Ab Initio* Calculations and Ellipsometry Measurements

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Similar to inorganic semiconductors, hybrid perovskites have shown low exciton binding energies[1] (≈ 5-30 meV) suggesting a potentially high relative dielectric constant (ε ≈ 70) at low frequencies. Understanding the physics of the excitons in these materials is crucial in order to increase the charge extraction and improve the solar cells' efficiency.

In this work, 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 $CsPbI_3$ are derived using the linear response approach (DFPT). As for the orthorhombic phase of $CsPbI_3$, we find a very flat energy profile around its equilibrium structure (figures 1, 2), indicating strong anharmonic effects. The results obtained (static ε around 20) are coherent with low exciton binding energies, and go against the possibility of a giant dielectric constant for these hybrid perovskites, which had been reported at very low frequencies (<1 Hz) (ε ≈ 1000 in the dark[2]). The dielectric properties (ε versus frequency) obtained for $CH_3NH_3PbI_3$ show good agreement with the ellipsometry measurements we performed in collaboration with Horiba Jobin Yvon company.

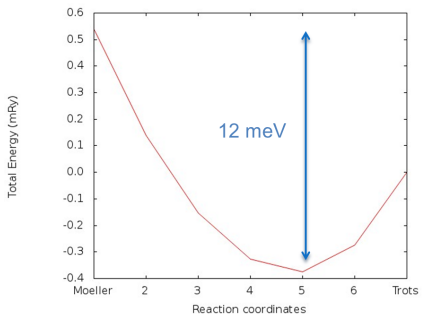

Figure 1: Equilibrium energy of $CsPbI_3$'s orthorhombic phase (T<530K). The 5 intermediate position sets are linearly interpolated between sets 1 (*Moeller*) and 7 (*Trots*) which are equilibrium positions relaxed from experimental initial structures [3,4].

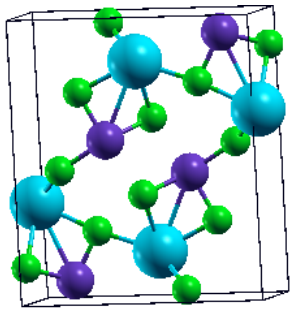

Figure 2: Equilibrium structure of $CsPbI_3$ in its orthorhombic phase for position set 5. The atomic positions are relaxed, and the blue, purple and green atoms respectively denote Cs, Pb and I.

References

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