

Black Phases of CsPbI₃: Structural and Theoretical Studies

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In less than 10 years, hybrid organic-inorganic perovskites have emerged as a new generation of absorber materials for high-efficiency and low-cost solar cells [1], [2]. More recently, fully inorganic perovskite quantum dots (QD) also led to promising efficiencies [3], [4] and then become a serious alternative to hybrid organic-inorganic perovskites. Currently, the record efficiency for QD solar cells is obtained with CsPbI₃. High resolution in-situ synchrotron XRD measurements have been performed on CsPbI₃ as a function of the temperature and revealed a highly anisotropic variation of the lattice parameters. Moreover, CsPbI₃ can be temporarily maintained in a perovskite-like structure down to room temperature, stabilizing a metastable perovskite polytype (black-phase) crucial for photovoltaic applications. Structural, vibrational and electronic properties of the three experimentally observed black phases are further scrutinized using theoretical approaches [5], [6]. A symmetry-based tight-binding model, calibrated with self-consistent GW calculations including spin-orbit coupling, affords further insight into their electronic properties. A Rashba effect is thus predicted for both cubic and tetragonal phases when using the symmetry breaking structures obtained through frozen phonon calculations.

[1] A. Kojima, et al., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* 2009, 131, 6050–6051.

[2] Best research-cell efficiencies; <https://www.nrel.gov/pv/assets/images/efficiency-chart.png> (accessed Nov 7, 2017).

[3] H. Bian et al., Graded Bandgap CsPbI₂+xBr_{1-x} Perovskite Solar Cells with a Stabilized Efficiency of 14.4%, *Joule* (2018), <https://doi.org/10.1016/j.joule.2018.04.012>

[4] E. M. Sanehira, et al., Enhanced Mobility CsPbI₃ Quantum Dot Arrays for Record-efficiency, High-voltage Photovoltaic Cells. *Sci. Adv.* 2017, 3, eaao4204.

[5] A. Marronnier et al., Structural Instabilities Related to Highly Anharmonic Phonons in Halide Perovskites. *J. Phys. Chem. Lett.* 2017, 8, 2659–2665

[6] A. Marronnier et al., Anharmonicity and Disorder in the Black Phases of Cesium Lead Iodide Used for Stable Inorganic Perovskite Solar Cells. *ACS Nano* 2018, 12, 3477–3486

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