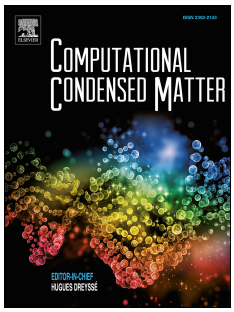
Accepted Manuscript



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PII: S2352-2143(17)30261-7

DOI: 10.1016/j.cocom.2018.02.001

Reference: COCOM 137

To appear in: *Computational Condensed Matter*

Received Date: 13 November 2017

Revised Date: 1 February 2018

Accepted Date: 1 February 2018

Please cite this article as: A. Koliogiorgos, S. Baskoutas, I. Galanakis, Electronic and gap properties of Sb and Bi based halide perovskites: An *ab-initio* study, *Computational Condensed Matter* (2018), doi: 10.1016/j.cocom.2018.02.001.

Electronic and gap properties of Sb and Bi based halide perovskites: An *ab-initio* study

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Abstract

Halide perovskites are currently under intense investigation due to their potential applications in optoelectronics and solar cells. Among them several crystallize in low symmetry lattice structures like trigonal, hexagonal, orthorhombic and monoclinic. Employing *ab-initio* electronic structure calculations in conjunction with generalized gradient approximation and hybrid functionals we study a series of perovskites with the formula $A_3B_2X_9$ which have been grown experimentally. A stands for a monovalent cation like Cs, Rb, K or the organic methylammonium molecule (MA), B is Sb or Bi, and X is a halogen. Moreover we include in our study both the effect of spin-orbit coupling in the halide perovskites and the influence of the orientation disorder of the MA cation on the energy band gaps of these compounds. Most compounds under study exhibit absorption in or close to the optical regime and thus can find application in various optoelectronic devices. Our results pave the way for further investigation on the use of these materials in technology relevant applications.

Key words: Halide perovskites, Density-functional theory, Electronic Band structure
PACS: 71.20.-b, 71.20.Nr, 71.15.Mb

1. Introduction

The continuous growth of energy consumption and the finite amount of available fossil fuels has triggered the research on alternative energy sources and especially the so-called "renewable energy sources". Among them sun is the most promising since it is an infinite energy sources and solar cells are under intense study. The most widely used material for solar cells is silicon with a history of over 60 years [1]. But the search for new cheap, earth-abundant materials, which can substitute silicon in solar cells, is at a peak in recent years [2]. Among the proposed materials, perovskites [3] consist a promising family of materials for the photovoltaic (PV) industry [4–6]. Research on perovskites for PVs has still to address multiple issues like efficiency (PCE), the width of the energy band gap, that needs to correspond roughly to the visible spectrum, and device stability in ambient conditions prior to their commercial use. The interest on the family of perovskites also embraces other technological important research regions like optoelectronic devices [7] and catalysis [8].

Early perovskites contained oxygen and had the general structure of ABO_3. To achieve charge neutrality, A has to be a cation of +2 valence and B a cation of +4 valence of dissimilar size like in $CaTiO_3$ [9]. Latter it was found that in the same family of compounds an increasing number of materials can be categorized [5,6]. First, one can use halogen atoms instead of oxygen, giving birth to the so-called halide perovskites [10] Charge neutrality implies now that A is a monovalent cation and B a divalent.The A cation does not have to be a pure element but also an organic molecule and in this case the materials