

Ag-Bi-I rudorffites for solar-cell applications: Insights on their structures, electronic and optical properties from first-principles

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Lead halide perovskites exhibit excellent photovoltaic properties and over the past years have revolutionized the field of solution processed photovoltaics, achieving record power conversion efficiencies (PCE) of above 25.5% [1]. Yet, due to concerns raised regarding the presence of the non-environmentally friendly Pb-atoms, the quest for stable non-toxic materials with high photo-conversion efficiency remains an active topic of research. In 2017, silver bismuth halides with an $A_aB_bX_x$ ($x = a+3b$) lattice [2], were shown to be highly stable and promising candidate materials for solar cell applications. These compounds, also called rudorffites, exhibit optical band gaps ranging between 1.4 eV to 2.0 eV [3], impressive high short-circuit current [4,5] and have achieved PCE of up to 5.6% [6]. Contrary to perovskites, these materials exhibit edge-shared AX_6 and BX_6 octahedra hence breaking the paradigm of corner-sharing structures for good opto-electronic properties. Furthermore, these materials have an ease of processing and can be synthesized by spin-coating techniques [7], thermal co-evaporation [8], as well as through solution atomization to produce aerosols [9]. The compounds can be defined as a joint population between three types of sites: vacant-sites Δ , monovalent and trivalent cation sites, which each of these can exhibit different occupancy depending on the relative monovalent/trivalent atom ratio [5]. This mixture of atomic sites with variant occupancies, make rudorffites particularly difficult to model. In fact, to-date a systematic investigation of their structural, electronic and optical properties is missing. In this work, we thoroughly analyse the symmetry of the rudorffites structures and employ state-of-the-art calculations from first-principles to unveil their electronic and optical properties. We highlight the full class of materials, and focus on the previously synthesised Ag_3BiI_6 , $AgBiI_4$ and $AgBi_2I_7$ [5]. We begin with $AgBiI_4$, which corresponds to a 50% Ag/Bi ratio, and use the symmetry groups associated with this material (i.e., $R3m$, $C2/m$ and $Fd3m$) to show that it is a necessary requirement to model the materials in subgroups of these in order accurately describe the lattices. To do so, we use the so-called Wyckoff splitting method, which allow us to unveil the fine details of the electronic band structure of the material, and accurately compute its electronic band-gap. Having established a computational model to look at these compounds, we move on, to examine the case of Ag-rich compounds by looking at Ag_3BiI_6 . We report a dramatic improvement in the absorption spectra of the material, and explain this improvement by analysing the atomic orbital associated with the photo-active transitions. Overall, we explore the rudorffite materials phase-space and propose the key atomic-scale parameters that can allow tuning and optimizing the opto-electronic properties of these compounds that are critical for their photovoltaic applications.

Acknowledgments

The research leading to these results has received funding from the Chaire de Recherche Rennes Metropole project, and from the European Union's Horizon 2020 program, through a FET Open research and innovation action under the grant agreement No 862656 (DROP-IT). This work was granted access to the HPC resources of TGCC under the allocations 2020-A0100911434 and 2020-A0090907682 made by GENCI. We acknowledge PRACE for awarding us access to the ARCHER2, United Kingdom.

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