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Influence of surface ligands on the electronic properties of AgBiI₄ rudorffites nanocrystals

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In the last decade, owing to a combination of outstanding optical and electronic properties, lead halide perovskite (LHP) have prevailed as promising low-cost materials for optoelectronic applications going from photovoltaics¹ to photocatalysis². However, within a time when ecology is the keystone of concerns, the presence of lead at the forefront of their structures and properties, as well as their operational instability, hindered their commercial applications^{3,4}.

In the sake of non-toxic alternatives, Ag-Bi-I Rudorffites have recently emerged as potential candidates. Indeed, in 2016, solar cells made from these materials showed a power conversion efficiency of 1.2%⁵, which has now increased to 5.4%⁶. With edges-shared AgI₆ and BiI₆ octahedra, Rudorffites have well-positioned band gap and high absorbance in the entire visible range, along with greater stability in ambient conditions than LHP⁶.

In this study, AgBiI₄ nanocrystals (NCs) have been synthesized via the hot-injection route. Interestingly, they show a quasi-direct band gap value closely matching the bulk material one. Alongside, surface characterization has shown the presence of ligands passivating the NCs' surface, suggesting an effect of the surface coverage on the electronic properties. Recent theoretical developments based on density functional theory (DFT), have uncovered the influence of surface dipoles on work functions in LHP⁷ and similar mechanisms might occur here. Up to date, this has not been demonstrated yet for Ag-Bi-I Rudorffites NCs. Therefore, expanding recent theoretical descriptions of Ag-Bi-I Rudorffite bulk properties⁸, we propose to combine DFT surface calculations with experimental results, to clarify the fundamental mechanisms behind the bandgap closing observed in these nanocrystals.

References

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