Excitonic Properties of Vacancy Ordered Halide Double Perovskites: From Wannier to Frenkel excitons

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Over the past decade ABX_3 halide perovskites based on Pb have emerged as a most-promising class of materials. To-date they have been employed for record-breaking solar-cells[1], highly-efficient light-emitters[2], new photo-catalysts[3] and even as X-ray detectors[4]. A_2BX_6 vacancy ordered double perovskites (VODP) are air-stable and environmentally friendly (Pb-free) that have been proposed as alternatives[5], to halide perovskites. Yet, VODP materials have not achieve the high performance of their Pb-based counterparts. In this work, we thoroughly analyze the properties of the VODP family of materials by employing state-of-art ab initio calculations to unveil the key details of the electronic structure and the effects of electron-hole coupling on the optical properties.

We sample the VODP structures by picking prototypes accordingly to the electronic configuration of the tetravalent metal at the B-site, which is known to dominate the electronic properties of these materials alongside the halogen species. In particular, we select the known materials[5,6,7] Cs_2TeX_6, Cs_2SnX_6, and Cs_2ZrX_6 (with X=Br, I). The structural properties are first investigated, and show how the size of the vacancy, is in fact tuned solely by the size of the halogen. We assess the mechanical stability of each crystalline lattice by means of phonons calculations. The electronic structures are investigated within the GW many-body green's function method, where we discuss the effects of the substitutional engineering on the dispersion of the electronic bands, and relate our findings to the expected charge carrier mobilities of each type of VODP. The optical and excitonic properties of these compounds are investigated by solving the Bethe-Salpeter equation (BSE) and are directly compared with the available experimental data. We report the exciton binding energies and dark-bright exciton exchange splitting for each type of VODP. Finally, we address the exciton symmetries by performing a complete symmetry analysis of the compound's band structure and excitonic wavefunctions, on which a direct link between these and the metal site species is established.

Overall, we explore comparatively the role of electron-hole coupling and GW quasi-particles in VODP materials, and explain its correlation with the choice of the B-metal and X-halide sites. We show that the formation of excitons dominates the optical properties of the VODP perovskite family of materials and its properties can be tuned by both metal and halide composition. These results shed light on the suitability and the prospect of VODP type might exhibit, due to their opto-electronic and excitonic properties. Finally, we identify the most and least promising materials that could act as photo-active materials or for selective charge transport layers in light-emitting and solar-cell applications.

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