VERSATILITY OF HALIDE PEROVSKITES: INSIGHT FROM ATOMIC SCALE MODELLING

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ABSTRACT

Both all inorganic and hybrid halide perovskites have recently demonstrated undeniably remarkable characteristics for a wide range of optoelectronic applications. The perovskite fever began with 3D halide perovskites of chemical formula AMX_3 with A a small organic (e.g. methylammonium, formamidinium) or an inorganic cation (e.g. Cs^+), M a metal (Pb^{2+}, Sn^{2+}, Ge^{2+}), and X a halogen (I^-, Br^-, Cl^-), which have opened a route toward low-cost manufacture of solar cells while offering currently certified conversion efficiencies over 24%, at the level of the best known thin film technologies and not far from monocrystalline silicon (25%).[1] Since the initial breakthrough mid-2012,[2] halide perovskites have attracted worldwide efforts from the scientific community[3] leading to an extensive exploration of their structural versatility and an ever-growing diversity of structures.[4] Prior to the perovskite fever, especially in the 80's and 90's, most experimental efforts on halide perovskites were focused on chemistry and optical characterizations of monolayered halide perovskites of chemical formula $A'MX_4$, with A' a larger organic cation (e.g. alkylammonium).[5]

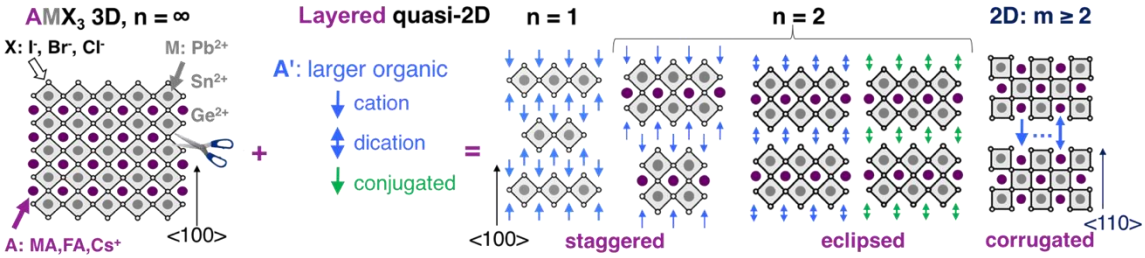

Figure 1. *Layered metal-halide structures conceptually derived from the mother 3D perovskite network.*

Currently, many different perovskite -with corner-sharing octahedra- as well as non-perovskite metal-halide networks are synthetized and their optoelectronic properties deserve to be unraveled (Figure). Among others, new compositions such as $A'_2A_{n-1}M_nX_{3n+1}$ afford layered structures with a controlled number (n) of octahedra in the perovskite layer and thus offer an ideal platform for fundamental understanding.[6] Here, through a couple of recent examples including newly discovered halide perovskite phases as well as experimental data from the early 90's, we will discuss their optoelectronic properties based on first-principles calculations, semi-empirical and empirical modelling. Impact of composition and structural pattern on properties will be inspected, with particular emphasis on the effect of quantum and dielectric confinements on charge carriers and excitons.[6,7] Theoretical inspection of low energy states associated with electronic states localized on the edges of the perovskite layers will also be shown to provide guidance for the design of new synthetic targets[8] taking advantage of experimentally determined elastic constants.[9] Opportunities to engineer halide perovskite properties by considering dications or conjugated molecules in the interlayer will also be discussed.[10]

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