**First-principles study of carbon-doped Cu₂O and lead-free A₂ZrX₆ defect perovskites for optoelectronic applications**

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The development of new wide-bandgap semiconductors is critical for advancing transparent and optoelectronic device technologies. In this work, we report density functional theory (DFT) studies on two classes of wide-bandgap materials with enhanced potential for optoelectronic applications: (i) carbon-doped cuprous oxide (Cu₂O), and (ii) lead-free halide defect perovskites, A₂ZrX₆, where A is an organic cation and X is a halogen.

Cu₂O is intrinsically a p-type semiconductor due to the presence of Cu vacancies. In this study, we examine the effects of carbon doping, considering substitutional doping at the oxygen and copper sites, as well as interstitial incorporation, using PBE and PBE+U approaches. Our results indicate an enhancement of the p-type character when carbon substitutes for an oxygen atom. In contrast, substitution of a copper atom by carbon or interstitial incorporation of carbon leads to shallow donor defect states near the conduction band minimum (CBM), thereby introducing compensating n-type conductivity.

We also report results on the structural and electronic properties of lead-free, halide, “defect” perovskites of the form A₂ZrX₆. These systems hold significant potential for many optoelectronic applications due to their stability and tunable properties. Utilizing PBE and HSE06 functionals, we systematically investigate the impact of A-site cation and X-site halogen substitutions on the structural and electronic properties. Specifically, we consider A = ammonium (NH₄⁺), methylammonium (CH3NH3+), dimethylammonium ((CH₃)2NH2⁺), trimethylammonium ((CH₃)₃NH⁺), formamidinium (CH(NH2)2+), trimethylsulfonium (CH3)3S+) or phosphonium (PH₄⁺); and X = Cl⁻, Br⁻, or I⁻. Our calculations reveal that both A-site and X-site substitutions significantly affect the band gap and the lattice parameters. Increasing the size of the A-site cation generally enlarges the unit cell, while halogen electronegativity directly correlates with the band gap, yielding the lowest values for iodine-containing systems and methylammonium cation in the A-site. We predict a wide range of band gaps (from ~4.79 eV for (PH₄)₂ZrCl₆ down to ~2.11 eV for MA₂ZrI₆, using HSE06).

Our first-principles predictions for C-doped Cu2O and Zr-based defect perovskites highlight their potential as next-generation semiconductors with tunable optoelectronic properties.

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