Unlocking New Light with Inorganic Perovskites Polymorphs

$CsMX_3$ (M = Ge, Sn or Pb; X = F, Cl, Br or I) inorganic perovskite polymorphs: excitons and optical absorption spectra

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In Short

- In this project, we will investigate excitons and the optical absorption spectra across a family of 12 $CsMX_3$ inorganic perovskites (where M = Ge, Sn, or Pb; X = F, Cl, Br, or I), each considered in 7 different geometries.
- We will solve the Bethe-Salpether equation (BSE), the state-of-the-art approach for modeling optical properties by explicitly accounting for electron-hole interactions.
- With this systematic study, we will gain a detailed understanding of how compositional variation and structural polymorphism can be leveraged to tailor absorption spectra and exciton properties.

Inorganic perovskites have attracted significant attention in recent years due to their excellent optoelectronic properties, which make them suitable for applications in solar cells, light-emitting devices, photodectors, thermoelectric converters, and even in emerging quantum computing technologies [1]. However, some of the most relevant perovskites, such as $CsPbI_3$, suffer from issues related to rapid degradation and lead (Pb) toxicity. As a result, alternatives have been actively sought. These include replacing Pb with less toxic elements like Sn or Ge, substituting I with other halogens (F, Cl, or Br), and experimenting with different crystal structures (polymorphs). In this context, a theoretical study capable of evaluating a broad range of inorganic perovskites is highly valuable, as it can guide the synthesis of the most promising candidates, targeting specific applications. Of course, such exploratory work should retain two critical aspects: predictive accuracy and computational efficiency. Unfortunately, these two aspects are usually hard to achieve simultaneously.

While density-functional theory (DFT) is well suited for addressing structural properties and thermodynamic stability, a more accurate description of electronic and optical properties often requires more sophisticated methods, such as a GW and the Bethe-Salpeter equation (BSE). This combination of GW+BSE is widely recognized as the state-of-the-art in theoretical modeling of optical properties in solids and molecules. Nevertheless, despite the remarkable accuracy that can be achieved with GW, its high computational cost, often surpassing that of BSE, can become a major bottleneck, particularly in large-scale or exploratory projects, involving many materials or structural variants. An alternative approach is the DFT-1/2 method. It can approximate GW at a fraction of the computational cost [2], and has already proven to be effective for calculating band gaps of perovskites [3].

In this project, we will replace GW with DFT-1/2, and combine it with BSE calculations. This strategy will enable an extensive investigation of excitonic and optical properties across a total of 84 perovskites with the general chemical formula $CsMX_3$, where M = Ge, Sn, or Pb, and X = F, Cl, Br, or I. For each of the twelve different compositions, we will consider 7 seven distinct crystallographic phases (cubic, tetragonal, orthorhombic, and rhombohedral; see Fig. 1). Through this extensive study, we aim to understand how both chemical composition (choice of metal and halide) and crystal structure affect the optoelectronic behavior of $CsMX_3$ perovskites. Ultimately, the insights gained will allow us to identify the most promising material candidates for applications in photovoltaics, ultraviolet detection, and light-emitting devices.

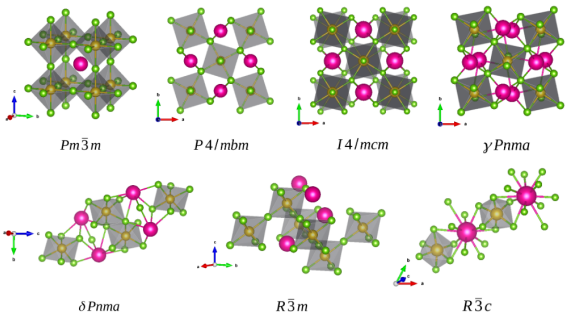

Figure 1: *Illustration of the seven different crystal structures for the $CsMX_3$ perovskites in this project: $Pm\bar{3}m$ (cubic), P4/mbm and I4/mcm (tetragonal), γ- and δ-Pnma (orthorhombic), $R\bar{3}m$, and $R\bar{3}c$ (rhombohedral). Extracted from Ref. [4].*

More Information

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[4] D. Nazaré de Freitas, C. R. da Silva, J. S. de Sousa, L. K. Teles, and M. Marques, *Chemical and structural trends on stability and electronic properties of CsMX3 (M = Ge, Sn or Pb; X = F, Cl, Br or I) inorganic perovskite polymorphs including relativistic and quasiparticle effects*, 2025, Submitted for publication; Under review.

DFG Subject Area

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