Electronic Band Structure Calculation of All-Inorganic Perovskites $CsAB_3$, with A: Pb, Sn, or Ge, and B: I, Br, or Cl

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ABSTRACT

This research focus the análisis of $CsAB_3$ full inorganic halide perovskites, with a specific focus on bandgaps, lattice parameters, and formation energy for optimizing Perovskite Solar Cells (PSC). Given the environmental concerns associated with lead (Pb), this study seeks to analyze these structures by substituting lead with more eco-friendly alternatives such as tin (Sn) and germanium (Ge). Ab-initio calculations based on Density Functional Theory (DFT) and the Full-Potential Linearized Augmented Plane-Wave method (FP-LAPW) in VASP code are employed. The study includes lattice parameter, band gap, and formation energy analyses for $CsAB_3$ perovskites, where A represent elements such as Sn or Ge as substitutes for Pb and the hallide B = Cl, Br, or I. Four key results are presented: (Figure 1) correlation between experimental and DFT lattice parameters, (Figure 2) band gaps, (Figure 3) linearity between DFT SCAN results and Machine Learning approximation, and (4) formation energy of Cl, Br, and I perovskites with Pb, Sn, and Ge substitutions.

INTRODUCTION

Perovskite Solar Cells (PSC) show promise for cost-effective photovoltaics. This research focuses on $CsAB_3$ perovskites, exploring substitutions of Pb with Sn or Ge to reduce lead content. Critical parameters include band gap, lattice parameters, and formation energy, influencing PSC efficiency and stability. The motivation for this research stems from environmental concerns related to lead, prompting an investigation into more eco-friendly alternatives like tin and germanium. Ab-initio calculations using Density Functinal Theory (DFT) provide insights into material properties.

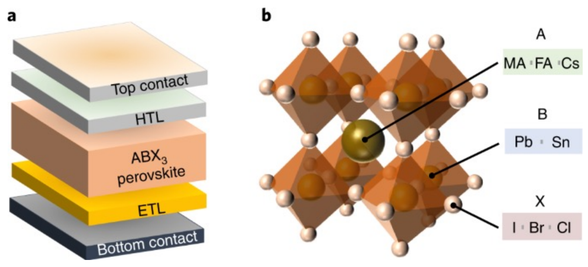

Figure 1. a) Solar Cell Schematic. b) Crystal structure $CsAB_3$

The calculation of the electronic properties of these materials, especially compounds based on lead or organic composition, has attracted attention from various previous scientific studies. For instance, Figure 1 from the research conducted by Tao, S., Schmidt, I., Brocks, G. et al., compares the band gaps of 18 different perovskites.

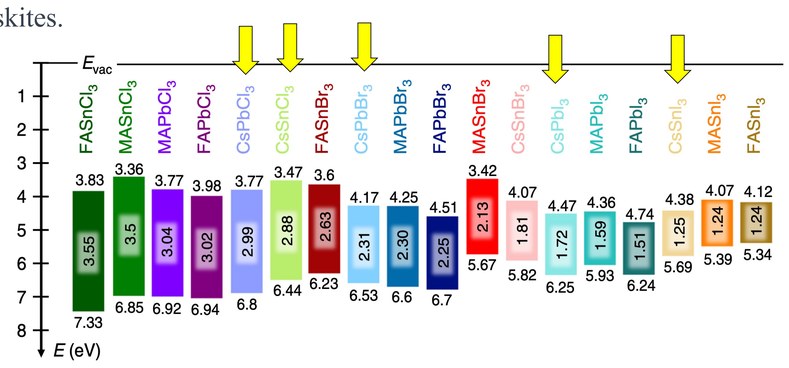

Figure 2. Schematic energy level diagram of the 18 metal halide perovskites. The respective IE and EA values as well as the optical gaps (all in eV). (Tao, S., Schmidt, I., Brocks, G. et al.).

METHODOLOGY

- All calculations were performed in the framework of the Density Functional Theory (DFT), using the pseudopotential and plane wave method (VASP).
- The exchange-correlation functional was described using the SCAN parametrization of the metaGGA approach.
- The cut-off energy was set to 500 Ry, and the reciprocal space described by a dense 13x13x13 k-mesh.
- All compounds were considered with space group Pm-3m (221), where the lattice parameters has been optimized.
- Machine learning (ML) method has been used in order to compare with DFT calculations, for future research for different concentration of atomic substitution.

RESULTS

Correlation between Experimental and DFT Lattice Parameters:

Our computational models have been validated by comparing experimentally determined lattice parameters with those calculated through DFT.

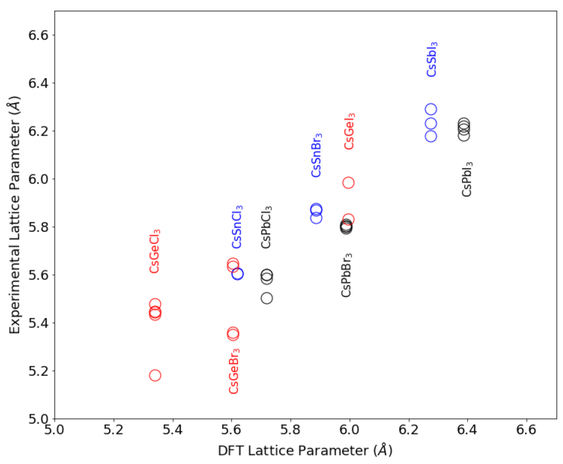

Figure 3. Correlation between experimental values and DFT Lattice Parameter

Band Gaps for Compounds with B = Ge, Sn and Pb, X = Cl, Br, or I:

The second graph shows the band gaps of $CsAB_3$ perovskites with X = Cl, Br, or I, providing crucial information for optimizing energy conversion efficiency of PSCs using computational simulations software.

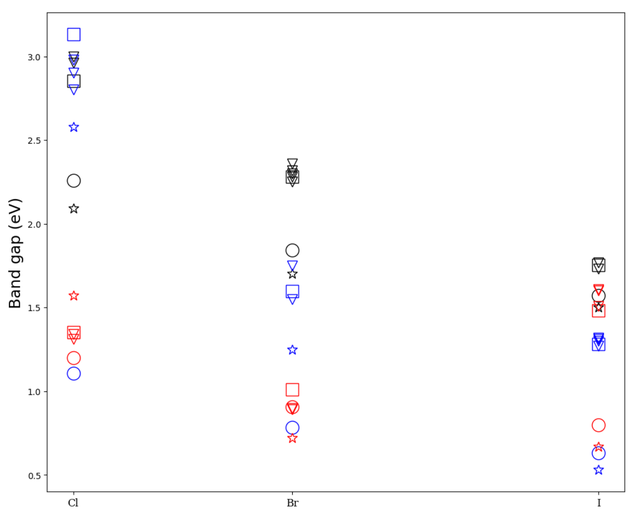

Figure 4. DFT Electronic Band Gap of the compounds CsAB3.

Linearity between DFT SCAN Results and Machine Learning Approximation:

The third graph showcases the linear relationship between DFT SCAN results (in eV) and a Machine Learning approximation. This correlation demonstrates the predictive accuracy of the employed computational method, additionally, in the stripe represents the range of the effective bandgap for solar energy harvesting. The yellow stripe in the figure 4 represents the effective range of band gap to be used for solar energy harvesting in PSC.

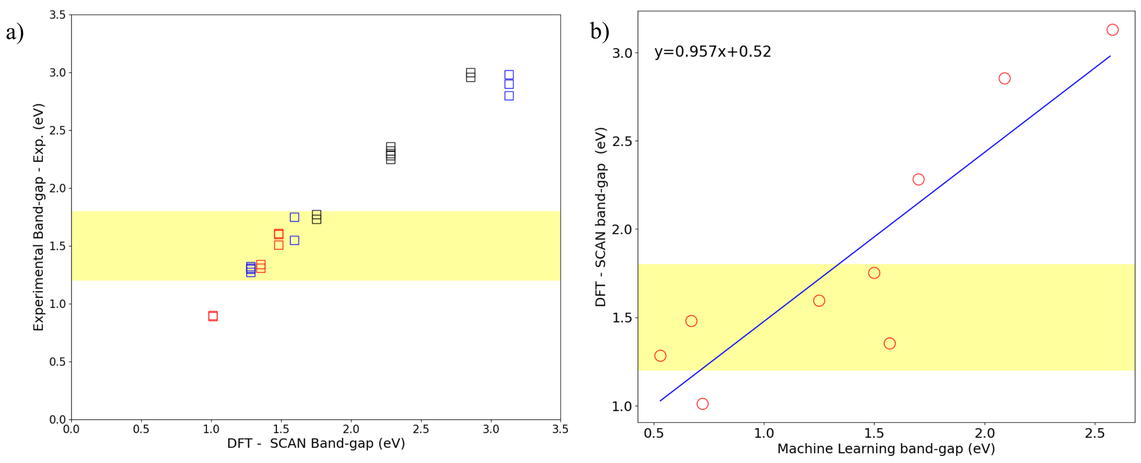

Figure 5: a) linear correlation between DFT and experimental bandgap values. b) Correlation between DFT and ML band-gap.

Formation Energy of $CSAB_3$ with Pb, Sn, and Ge Substituted Perovskites:

The final graph displays the formation energy of $CsAB_3$ perovskites with Cl, Br, and I, considering Pb and substitutions with Sn and Ge. These results provide insights into the stability and viability of alternative compositions for PSC.

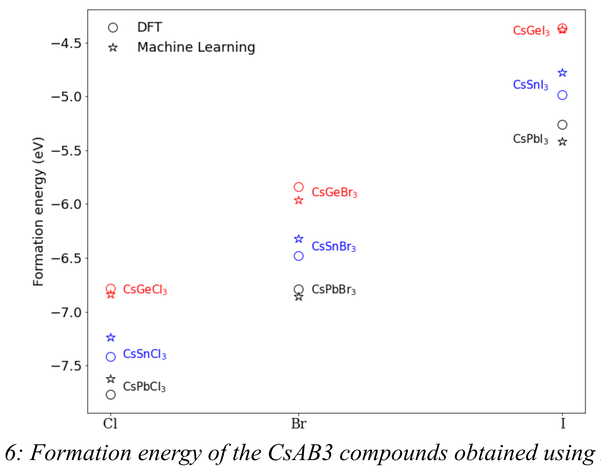

Figure 6: Formation energy of the CsAB3 compounds obtained using DFT and ML.

CONCLUSIONS

- New lead-free materials for solar energy harvesting in PSC were studied.
- DFT calculations demonstrated a strong linear correlation with experimental data for structural properties and band gaps.
- Significant correlations between machine learning techniques and DFT were found.
- This results enables the study of different combinations such as $CsA_{1-x}A'_xB_{3-x}B'_x$, where A, A' = Pb, Ge, and Sn; B, B' = I, Cl, Br.

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