First-principles computational study of highly anharmonic chalcohalide anti-perovskite materials for energy applications

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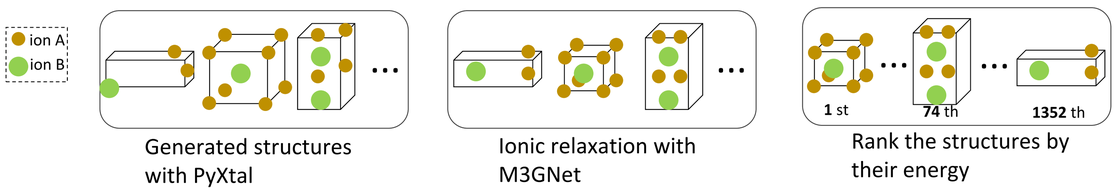
ABSTRACT

Chalcohalide anti-perovskites are a family of inorganic materials with chemical expression Ag_3BC, where B=S, Se, and C=Br, I. These compounds were synthesized and experimentally characterized several years ago [1,2], however, a detailed description and understanding of the phase competition and structural and optoelectronic properties is still lacking, both at the experimental and theoretical levels. These materials are expected to present suitable functional properties for optoelectronic and energy applications [3]. In this work we present a comprehensive computational study of these compounds based on first-principles methods (DFT), and we compare them with recent experimental results [4], obtaining strong agreement between theory and experiments in both, structural and optoelectronic properties. A in-house code for crystal structure prediction is also presented, this method uses random search algorithms and machine learning interatomic potentials to find low energy phases for a desired material in short timeframes and in a personal computer.

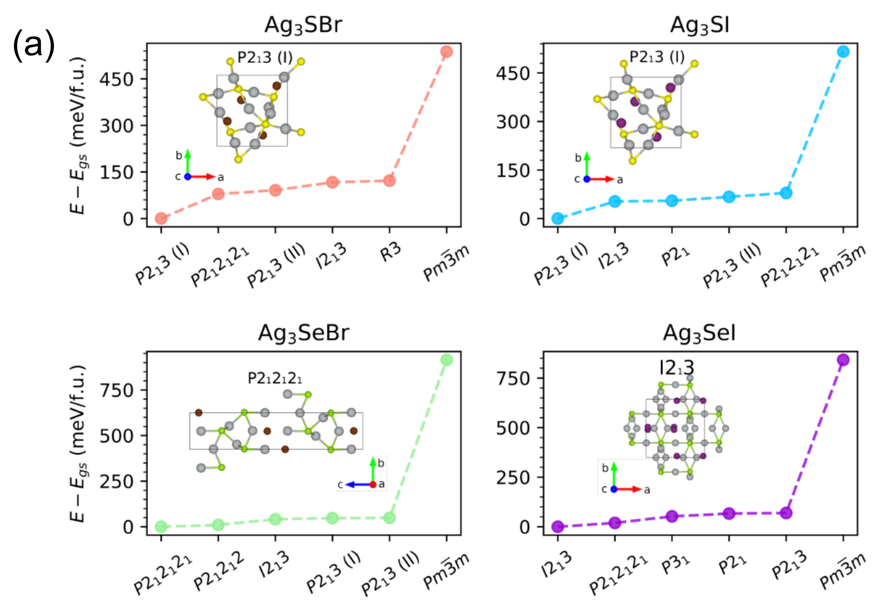
CRYSTAL STRUCTURE PREDICTION

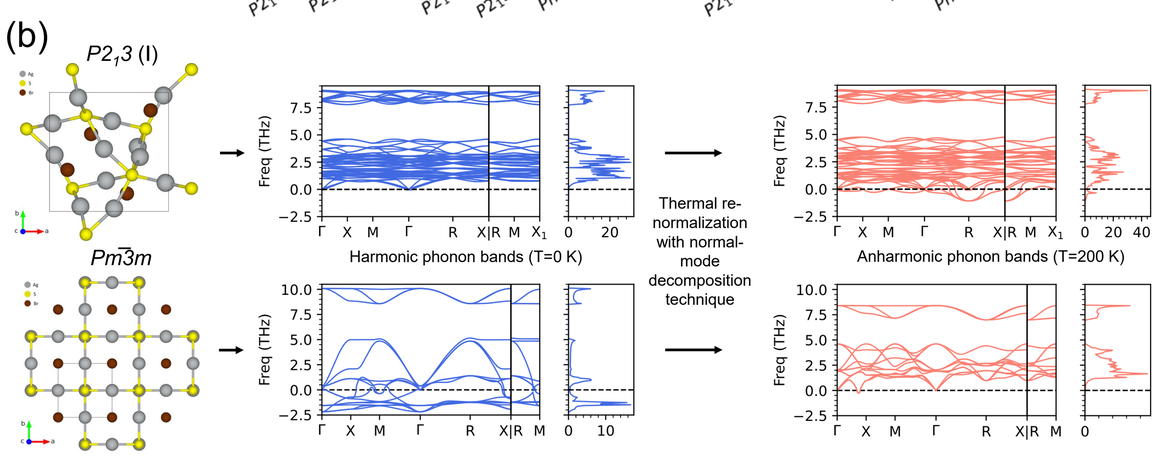
The positions that ions occupy in the unit cell and the ion type, fully determines the physical and chemical properties of materials. Ab-initio crystal structure prediction (CSP) aims to find low-energy phases for a given material, but this is a difficult problem [5]. We developed PyMCSP [6], a **Py**thon and **M**achine learning methods implementation for **C**rystal **S**tructure **P**rediction. This method generates structures with different point group symmetries, and perform ionic relaxation with machine learning interatomic potentials. By proceeding in this manner, we avoid the use of computationally intensive DFT calculations.

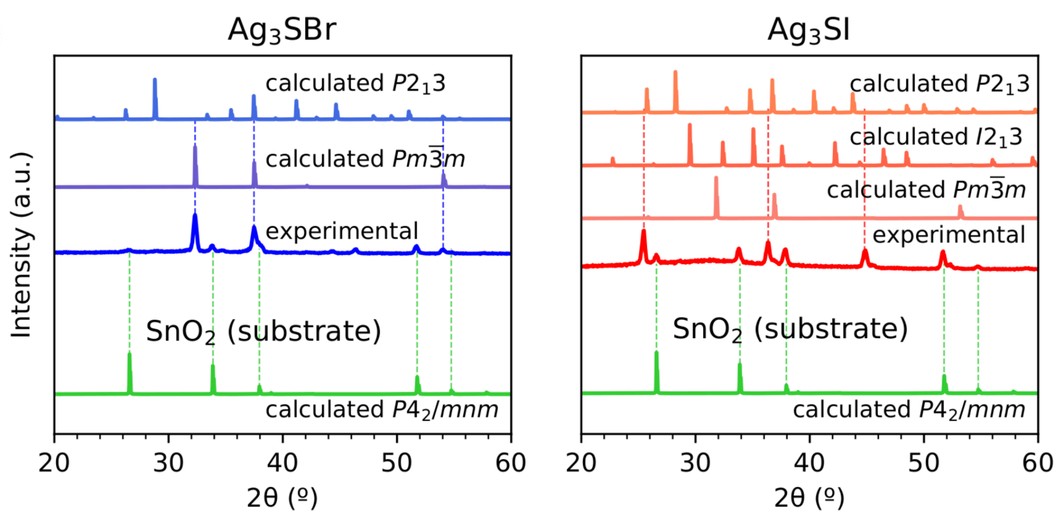


STRUCTURAL PROPERTIES

Study of the polymorphism and structural properties of chalcohalide anti-perovskites [7]. (a) Energy comparison for novel vibrational stable phases. (b) Phonon thermal renormalization for the ground-state and the room-temperature experimental phase, $Pm\bar{3}m$, for the Ag_3SBr compound. Superionic behavior was obtained at T=600 K. (c) X-ray diffractogram comparison between experimental and theoretical results.

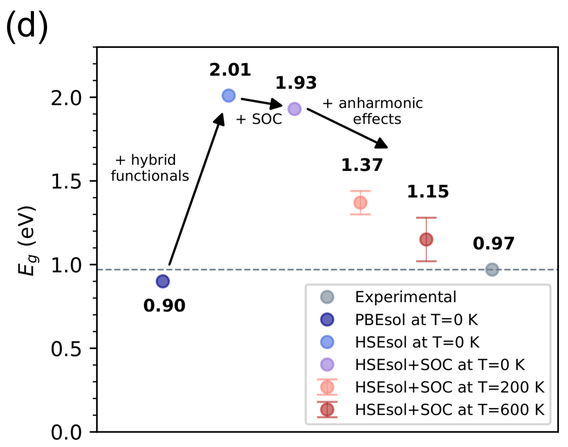


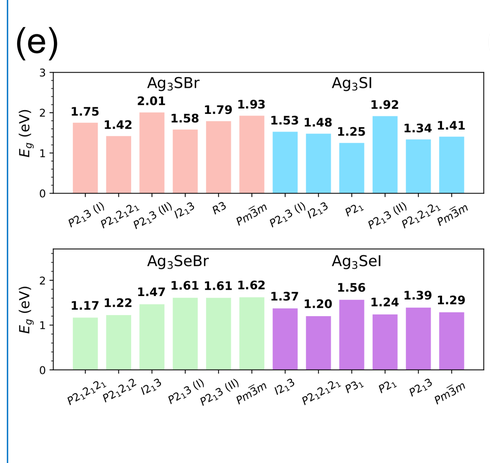


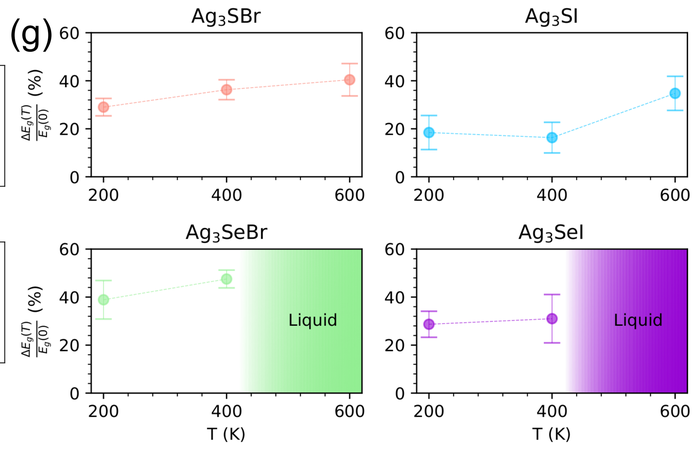


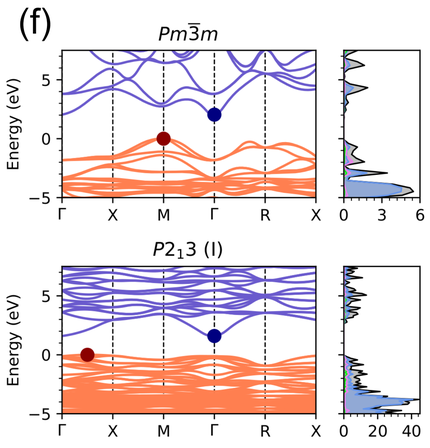
OPTOELECTRONIC PROPERTIES

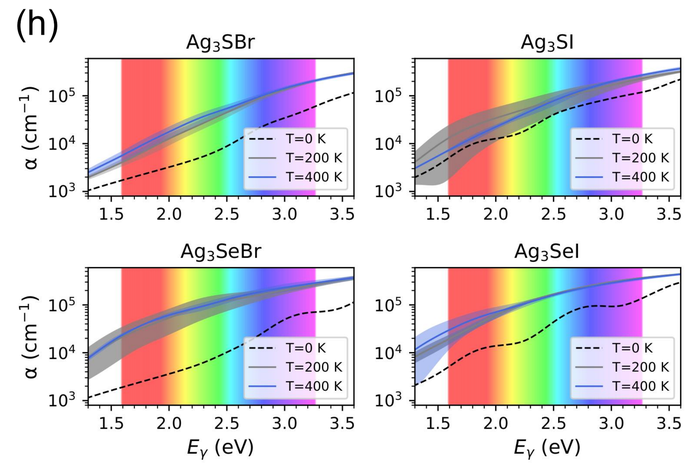
Study of the optoelectronic properties of chalcohalide anti-perovskites [8]. (d) Change in band gap with different levels of theory. (e) Band gaps and (f) energy bands (for Ag_3SBr) computed at T=0 K. (g) Band gap decrease with temperature for the room-temperature phase. (h) Absorption coefficient variation with temperature for the $Pm\bar{3}m$ phase. Suitable optoelectronic properties for absorbents in photovoltaics.











CONCLUSIONS

- Chalcohalide anti-perovskite compounds present high polymorphism, many novel vibrational stable phases discovered at T=0 K.
- The experimental room-temperature phase ($Pm\bar{3}m$) is non-vibrational stable at T=0 K, and we need anharmonic approaches.
- Superionic behavior expected at certain temperature between T=400 K and 600 K.
- Band gaps and optical properties suitable for optoelectronic applications.
- Giant effects of the thermal renormalization due to the anharmonicity for the optoelectronic properties.
- Materials interesting for solid state batteries and solar cells.

References

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