Effect of composition on the electronic, vibrational, and dielectric properties of inorganic halide perovskites: Insights from theory

Antoine Gissler[1, 2], Philip Schulz[3] and Philippe Baranek[1, 2]

[1] EDF R&D, Department SYSTEME, EDF Lab Paris-Saclay, 7 boulevard Gaspard Monge, F-91120 Palaiseau, France

[2] IPVF, Institut Photovoltaïque d'Ile-de-France, 18 Boulevard Thomas Gobert, 91120 Palaiseau, France

[3] IPVF, UMR 9006, CNRS, Ecole Polytechnique, IP Paris, Chimie Paristech, PSL, F-91120 Palaiseau, France

Nowadays, solar cells based on hybrid organic inorganic halide perovskites achieve record power conversion efficiencies of 26% and form the basis of tandem cells with efficiencies beyond 33%. However, the absorber materials exhibit stability issues in part owned to the volatile organic cations. An alternative seems to emerge, based on fully inorganic perovskites: corresponding devices reach efficiencies of up to 21% and seem to possess better stability. However, these materials have rich sequences of phase transitions associated in particular to the existence of soft phonon modes which can locally generate phase instabilities. In this work, the evolution of the electronic, vibrational, and dielectric properties of cubic inorganic halides perovskites based on germanium, tin and lead is systematically investigated at the first-principles level, using a hybrid exchange-correlation functional optimized to yield description of their structural, electronic, and phonon properties, in good agreement with experiment. The influence of the different ions on the phase stability of the cubic phase of ABX_3 (A= Li, Na, K, Rb and Cs, B = Ge, Sn, and Pb, and, X = Cl, Br and I) compounds is analyzed in terms of phonon mode stability, thermodynamic data, and correlated with the Goldschmidt tolerance factor (*t*), crystal distortions as well as the degree of hybridization in the bonds. We show that there is a correlation between *t* and the different lattice distortions involved in the phase transitions for which the perovskites, except for $CsSnX_3$, possess unstable modes for all *t* values meaning that the cubic phase is unstable. By varying the perovskites chemical composition, it was also possible to propose several structures with stability in the cubic phase. Together with the thermodynamic data and the electronic properties, as band gap and dielectric response, this provides a first set of criteria for optimizing the materials for different photovoltaic applications and for suggesting effective complex perovskites (see Figure 1).

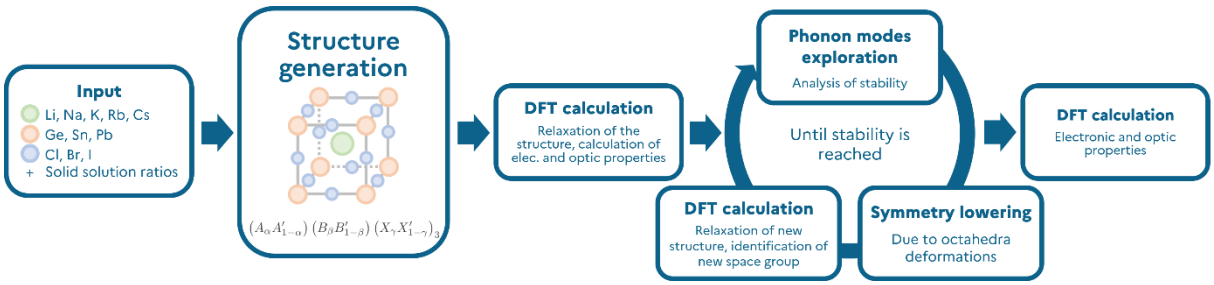

Figure 1 : Flowchart of the method used to determine the different atomic structures of the inorganic perovskites studied in this work.