

European XFEL Theory Seminar

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Campus Schenefeld, main building (XHQ) room E1.172

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General trends in thermodynamics of crystalline perovskites

Thermodynamics including the phase diagram of the crystalline perovskites is derived in terms of a multi-valley approach to their energy landscape vs. atomic displacements. It is shown how a certain pattern of non-collinear displacement order parameter leads to the formation of a local minimum for every structural phase in BaTiO₃, KNbO₃ and PtTiO₃ perovskites.

The derivation of the free energy for all phases is based on the vibrational entropy evaluated around each local energy minimum and involves the knowledge of the phonon spectra around the minimum for the entire range of the wave numbers, i.e. in the whole Brillouin zone. It is concluded that the local minimum of the thermodynamic phases including high-temperature non-polarized cubic phase can be captured if the unit cell is large enough to accommodate a spiral type displacement pattern. Perovskites with A-site cations of the ionic type such as BaTiO₃ and KNbO₃, demonstrate a priori trends toward the highly non-collinear off-centering of B-site cations of the octahedron-facet type, confirmed a posteriori by the diffuse X-ray scattering measurements done in the past. Non-collinearity is also a primary cause for a relatively modest tetragonal strain effect observed in alkali-based bulk perovskites. The displacement trends explain poly-morphic phase boundary (PPB) observed in alkali-based (AA')BO₃ perovskite compounds rather than morphotropic (MPB) range on the phase diagram desirable for practical applications. On the other hand, perovskite systems with high covalency on the A-site such as PbTiO₃ develop mostly collinear-type displacements of both cation types, which along with considerable coupling between strain and displacements explains anomalous electromechanical coefficient. Suggestions are made in terms of enhanced tetragonality and converting PPB to MPB by using certain stoichiometry in alkali-based perovskite systems. Microcanonical molecular dynamics simulations confirm finite-temperature trends for displacement patterns established within quasi-harmonic approximation and provide polarization values in agreement with experiment.

Host: Evgeny Gorelov