

Poster Presentation

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Phase Transitions in Borohydride Perovskites

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A series of complex hydrides based on the highly dynamic tetrahydroborate anion BH_4^- and crystallizing in the ABX_3 type lattice has recently been discovered. They present a rare case of a family of ionic-covalent hydrides that has a genuine tunable host lattice, making them an interesting new class of host compounds for not only the design of hydrogen storage materials but also hydride-properties related to heavy metals. Amongst these, preliminary results on *REE*-based luminescence will be discussed in the neat and doped compounds, the Ln^{2+} excited states surprisingly not being subject to significant quenching by B-H vibrations. Unlike oxide- or halide-perovskites some members of the $\text{AB}(\text{BH}_4)_3$ group do not evolve to higher symmetries as a function of temperature. We show by means of *in-situ* synchrotron X-ray powder diffraction, vibrational spectroscopy and *ab initio* calculations in the solid state, that temperature-induced structural distortions in perovskite-type $\text{ACa}(\text{BH}_4)_3$ ($A = \text{K}, \text{Rb}, \text{Cs}$) have their origin in close hydridic di-hydrogen contacts of repulsive nature. Coupling between internal B-H vibrations and phonons results in lattice distortions that are identical in symmetry to well-known instabilities (soft modes) in perovskites, which generally condense to lower temperatures. Anion-substitution $\text{BH}_4^- \leftrightarrow \text{X}^-$ ($\text{X} = \text{Halide}$) calculated on ordered models can relax distortions caused by repulsive effects. High temperature phase-transitions in $\text{ACa}(\text{BH}_4)_3$ can be of first or second-order, including 2-fold superlattices, simple cubic-cubic transitions accompanied by volume expansion or complex modulated superstructures accompanied by negative volume expansion, as is the case in $\text{RbCa}(\text{BH}_4)_3$. Close di-hydrogen contacts may be suggested as a tool to tailor the crystal symmetry in complex hydride perovskites in the future.

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