Theoretical prediction of decomposition paths for Ca(BH₄)₂ and Mg(BH₄)₂

YONGSHENG ZHANG, CHRIS WOLVERTON, ERIC MAJZOUB, VIDVUDS OZOLINS, MATERIALS SCIENCE & ENGINEERING, NORTH-WESTERN UNIVERSITY TEAM, PHYSICS & ASTRONOMY, UNIVERSITY OF MISSOURI COLLABORATION, MATERIALS SCIENCE & ENGINEERING, UNIVERSITY OF CALIFORNIA, LA COLLABORATION

Experimental and theoretical studies on Ca(BH₄)₂ indicate that the decomposition pathway of this compound is not a simple one-step reaction to final products, but instead may be a multi-step decomposition path (though the reaction pathway is currently unknown). We have studied the decomposition pathways of both Ca- and Mg-borohydride using Density Functional Theory (DFT) as well as a Monte Carlo-based crystal structure prediction method called PEGS. We find that a recently experimentally proposed CaB₂H₂ intermediate is extremely high in energy and hence very unlikely to form. We then symmetrically studied the low-energy structures of CaB₂H₄ and CaB₂H₆ stoichiometries by PEGS+DFT simulations. Based on all these possible reaction paths, the Ca(BH₄)₂ decomposition convex hull using our calculated reaction enthalpies finds a new compound, CaB₂H₆, which forms a nearly degenerate pathway to the previously-proposed CaB₁₂H₁₂ phase. Similar calculations for the Mg system show that the MgB₂H₆ predicted structure does not form a stable intermediate in the decomposition of Mg(BH₄)₂.

Yongsheng Zhang
Department of Materials Science & Engineering, Northwestern University

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