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Project H-31: Borohydride Materials Discovery and Development

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Background

Sandia/CA has been involved in hydrogen research, for over 40 years, and manages the USDOE Metal Hydrogen Center of Excellence. Hydride research at Sandia focused on complex hydrides for over 8 years, beginning with sodium alanate. More recently a combined effort of theory and experiment in materials searching and synthesis has yielded new metal hydride materials. New mixed cation materials based on AlH_n or BH_n anions are screened theoretically using a prototype electrostatic ground state (PEGS) method for generating low energy structures used in calculating the estimated enthalpy of decomposition. Synthesis methods involve mechanical alloying and a high pressure synthesis method employed at Sandia. This method utilizes compressed pellets of hydride precursor material, as well as potential catalysts, to exposure materials at pressures up to 2000 bar H_2, and temperatures up to 500°C.

Activities in 2007

We have continued our explorations of $Ca(BH_4)_2$, this year focusing on identifying crystal structures and exploration of reversibility in a collaborative effort with groups in the US and Europe. We had earlier shown that it is possible to prepare $Ca(BH_4)_2$ by reacting CaB_6 with CaH_2 if adding an additive, but higher pressures (i.e. 70MPa) were utilized. *In situ* synchrotron data collected at ESRF (in collaboration with Filinchuk, ESRF and Chandra, UNR) revealed the crystal structures of two polymorphs of $Ca(BH_4)_2$, labeled α-phase and β-phase, formed upon removal of solvent from $Ca(BH_4)_2{\cdot}2THF$, and a third polymorph, α'-phase, formed upon a second order transformation of the α-phase at 495K as also observed by DSC. The α'-phase changes into the β-phase upon heating above 453K and decomposes at 655 K into unknown products which according to TGA is associated with a weight loss, likely due to release of hydrogen. Another set of *in situ* synchrotron data collected at Brookhaven (in collaboration with Zhao et al of GE), revealed re-formation of $Ca(BH_4)_2$ after desorption, showing that this material is promising for reversible applications.

We are also exploring bialkali borohydrides. The four highest symmetry crystal structures from a PEGS search for $NaK(BH_4)_2$ are, from lowest to highest symmetry, *R*3, *R*-3, *P*3*m*1, and *R*-3*m*. Remarkably, all generated structures were trigonal. The total DFT energies, at T=0K, of the four structures are ordered monotonically with the crystal symmetry, with the highest symmetry *R*-3*m* having the lowest energy. The *P*3*m*1, *R*-3, and *R*3 structures have a T=0K total energy of 76, 80, and 110 meV above the R-3m structure, respectively. Using the lowest energy *R*-3*m* structure for $NaK(BH_4)_2$, and ignoring the phonon contribution to the total free energy, we have calculated the energy for the decomposition reaction of $NaK(BH_4)_2$ into $NaBH_4$ and KBH_4 to be near -3kJ/mol formula unit at T=0K. This indicates that the decomposition will proceed spontaneously. However, zero point energy (ZPE) phonon contributions can easily be larger than 3kJ/mol and the potential for a stable compound could not be ruled out initially. We were able to prepare this compound by high-energy mechanical alloying, and indeed, the phase is metastable and slowly decomposes. Rietveld refinements of experimental X-ray data confirmed the predicted structures. We are continuing exploring other bialkali borohydrides and also mixed alkali-transition metal borohydrides.

Published papers

1. Rönnebro, E.; Majzoub, E., Calcium Borohydride for Hydrogen Storage: Catalysis and Reversibility, J. Phys. Chem. B Letters, 2007, 111, 12045.
2. Filinchuk, Y.; Rönnebro, E.; Chandra, D., Crystal Structures and Phase Transformations in $Ca(BH_4)_2$, manuscript submitted.

Patent

1. E. Rönnebro, E. Majzoub, “Direct Synthesis of Calcium Borohydride”, U.S. Patent Application Serial Number 60/901,248 filed 02/12/2007.