complementarity is a widespread occurrence in the packing of molecules in crystals.

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Keywords: electrostatic potential, crystal engineering, intermolecular interactions

MS.46.1

Structure and properties of ammonia borane based hydrogen storage materials

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Ammonia borane contains more than 19wt% hydrogen and has received significant attention as a promising hydrogen storage material. Although the decomposition temperature of NH_3BH_3 is relatively low, its propensity to release deliterious decomposition products such as borazine has mitigated against its development as a hydrogen storage material. Here we present results that show that improved thermal desorption parameters may be obtained when one of the protic hydrogens on the nitrogen is replaced by either a lithium or a sodium cation. Lithium and sodium amidoboranes have recently been shown to release two molar equivalents of H_2 at around 92℃. Structural analysis has shown that both $LiNH_2BH_3$ and $NaNH_2BH_3$ are isostructural and that the dihydrogen bond that is evident in ammonia borane is not present in these amidoboranes. We present neutron and X-ray powder diffraction measurements and provide a detailed comparison of ammonia borane with the alkali metal amidoboranes and other amidoboranes that show promising decomposition behaviour close to room temperature.

Keywords: hydrogen storage, *in-situ* powder diffraction, neutron and X-ray diffraction

MS.46.2

Light metal borohydrides: Going beyond crystal structures

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Light borohydrides are considered as prospective materials for energy storage. However, due to their high stability they are not yet regarded being practical. In order to understand the stability and find ways to influence it we studied structure and transformations of some light borohydrides at various temperatures and pressures. New structures were solved from synchrotron powder diffraction data. Some complex cases include the simultaneous determination of a structure and a strong preferred orientation; solving a difficult structure in the space group $P1$; detection of the inversion symmetry breaking induced by ordering of hydrogen atoms. We show that hydrogen atoms can be accurately determined from synchrotron powder diffraction data measured with area detectors. Disorder of the borohydride groups and strong lattice anharmonicity were revealed from diffraction data measured at various temperatures. These phenomena, being ignored, lead to a failure of theoretical predictions

of structural stability of light borohydrides. Pressure-temperature phase diagram of $LiBH_4$ was studied by diffraction and mechanisms of phase transitions were analyzed using a phenomenological model. It suggests an existence of cation-anion layers in all four known $LiBH_4$ phases. This conclusion is not trivial from purely geometrical point of view, but it can find a rational crystal-chemical explanation. The relative complexity of $LiBH_4$ structures and of the P-T phase diagram can be linked with the directional interaction of the tetrahedral BH_4 groups with spherical metal atoms. We hypothesize that the directional $BH_4...M$ interaction in metal borohydrides leads to a formation of anion-centered complexes, determining structures of individual phases and mechanisms of their polymorphic transformations.

Keywords: hydride structure, synchrotron powder diffraction, structural transformations

MS.46.3

Structural investigation of metal borohydrides by X-ray/neutron diffraction and computational study

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Metal borohydrides, $M(BH_4)_n$ (M: metal; n: valence of M), are promising candidates for hydrogen storage materials because they have high hydrogen gravimetric capacity (ex. $LiBH_4$: 18.4mass%). Structural investigation of $M(BH_4)_n$ is an indispensable approach in order to understand their material properties. Whereas crystal structures of $M(BH_4)_n$ with n = 1 (alkali metal borohydride) have been clarified, those with n ≥ 2 are, in many cases, still uncertain. So far, we clarified new crystal structures of $Ca(BH_4)_2$ (space group $Fddd$ (No. 70) with a = 8.791(1) Å, b = 13.137(1) Å and c = 7.500(1) Å) [1], and $Y(BH_4)_3$ (space group Pa-3 (No. 205) a = 10.771(4) Å) [2], by using combination studies of powder x-ray/neutron diffraction and computation. Ca^{2+} and $[BH_4]^-$ arrangements of $Ca(BH_4)_2$ is a related TiO_2-type (anatase), and Y^{3+} and $[BH_4]^-$ arrangements of $Y(BH_4)_3$ is a distorted ReO_3-type. By using first-principles calculations based on the clarified crystal structures and estimated reactions $(1/2)Ca + B + 2H_2 = (1/2)Ca(BH_4)_2$ and $(1/3)Y + B + 2H_2 = (1/3)Y(BH_4)_3$, the heat of formation of $Ca(BH_4)_2$ and $Y(BH_4)_3$ were calculated to be -151 and -113 kJ/mol BH_4, respectively. They are in good agreement with the correlation between heat of formation for $M(BH_4)_n$ and number of Pauling electronegativity of M [3].

[1] K. Miwa *et al.*, (2006). *Phys. Rev.* B**74**, 155122.
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Keywords: hydrogen storage, neutron X-ray diffraction, density functional theory

MS.46.4

Powder diffraction investigations of a new class of rare-earth aluminum hydrides

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