

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

[1] M.A. Spackman, J.J. McKinnon, D. Jayatilaka, *CrystEngComm*, 10, 377-388 (2008)

Keywords: electrostatic potential, crystal engineering, intermolecular interactions

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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 deleterious 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°C . 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

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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 $\text{BH}_4\cdots\text{M}$ 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

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

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Metal borohydrides, $M(\text{BH}_4)_n$ (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 $M(\text{BH}_4)_n$ is an indispensable approach in order to understand their material properties. Whereas crystal structures of $M(\text{BH}_4)_n$ with $n = 1$ (alkali metal borohydride) have been clarified, those with $n \geq 2$ are, in many cases, still uncertain. So far, we clarified new crystal structures of $\text{Ca}(\text{BH}_4)_2$ (space group $Fddd$ (No. 70) with $a = 8.791(1)$ Å, $b = 13.137(1)$ Å and $c = 7.500(1)$ Å) [1], and $\text{Y}(\text{BH}_4)_3$ (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 $[\text{BH}_4]^-$ arrangements of $\text{Ca}(\text{BH}_4)_2$ is a related TiO_2 -type (anatase), and Y^{3+} and $[\text{BH}_4]^-$ arrangements of $\text{Y}(\text{BH}_4)_3$ is a distorted ReO_3 -type. By using first-principles calculations based on the clarified crystal structures and estimated reactions $(1/2)\text{Ca} + \text{B} + 2\text{H}_2 = (1/2)\text{Ca}(\text{BH}_4)_2$ and $(1/3)\text{Y} + \text{B} + 2\text{H}_2 = (1/3)\text{Y}(\text{BH}_4)_3$, the heat of formation of $\text{Ca}(\text{BH}_4)_2$ and $\text{Y}(\text{BH}_4)_3$ 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 $M(\text{BH}_4)_n$ and number of Pauling electronegativity of M [3].

[1] K. Miwa *et al.*, (2006). *Phys. Rev.* B74, 155122.

[2] T. Sato *et al.*, (2008). *Phys. Rev.* B77, 104114.

[3] Y. Nakamori *et al.*, (2006). *Phys. Rev.* B74, 045126.

Keywords: hydrogen storage, neutron X-ray diffraction, density functional theory

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

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The development of materials for the reversible storage of hydrogen in solid-state compounds is one of the most challenging topics for material scientists. Up to now, all systems investigated do not fulfill the requirements of a successfully working storage material. For this reason, research has to be expanded to new classes of materials. A new group of complex rare-earth aluminum hydrides was synthesized and characterized by X-ray powder diffraction methods. For the synthesis of the compounds, NaAlH_4 and the corresponding salts (XCl_3 with $\text{X} = \text{Pr, Nd}$) were ball-milled for several hours. The evaluation of the products show the formation of NaCl and Al during milling. Additionally to these phases, a set of new reflections is present, which is assigned to a new structure type of complex rare-earth aluminum compounds. The decomposition behavior of the rare-earth phases was investigated by in situ X-ray powder diffraction methods. During temperature increase, the new phases decompose above 120°C and rare-earth hydrides are formed. At higher temperatures, the hydrides decompose in a second step and the rare-earth elements react with free aluminum and e.g. NdAl_3 alloys are formed. The rehydrogenation behavior of the material was investigated by means of different in situ methods.

Keywords: hydrides, hydrogen storage, powder diffraction under non ambient conditions

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Neutron scattering studies on deuterium adsorbed pore framework compound, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$

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The biggest obstacle to realizing a hydrogen-energized vehicle is the on board hydrogen storage aspect. There are several different approaches to practically store/retrieve hydrogen in solid state systems. Amongst them, physisorption provides reversible and fast kinetics but works only at cryogenic temperature due to the weak binding energy between H_2 molecules and the storage material. In order to increase the adsorption enthalpy, metal-organic framework compounds $\text{A}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ ($\text{A} = \text{Na, K...}$) with coordinately-unsaturated alkali-metal ions were recently synthesized and yielded relatively high enthalpies. We have studied the H_2 loading mechanism in $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ using the neutron powder diffraction. Upon desolvation, the initial crystal structure was solved using the simulated annealing method. The K ion, found in the middle of relatively small pore, is coordinated by 5 N atoms of the surrounding cyano-groups forming a significantly distorted pyramidal configuration. Three sorption sites were identified around the K ion. The first binding site of D_2 is at the closest position sterically available to the K ions, with progressive sites filled in order of distance and steric plausibility. This leads us to the conclusion that H_2 molecules are strongly bonded to the site which provides the stronger polarizing power, if sterically accessible. In addition, we applied the maximum entropy method in order to confirm the loading sites that we found through the conventional Rietveld method. This statistical approach is meaningful, since we can not always obtain describe

locations of physisorbed-hydrogen well, in contrast to covalent/ionic compounds.

Keywords: neutron powder diffraction, *ab-initio* powder structure determination, hydrogen storage

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High pressure synthesis and physical property measurements of perovskite transition-metal oxides

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A breakthrough in materials has been often achieved triggered by discovery of a new key material. One of famous examples is the high-Tc superconductor which has opened new perspectives in physics, chemistry and materials science. Many other examples can be shown such as giant-magnetoresistant manganites, fullerene, carbon nanotube, MgB_2 superconductor, etc. Our institute has long history on high-pressure synthesis, and thanks to this we can use world highest class high-pressure apparatuses. Various unique structures do crystallize only with help of the high-pressure condition, which had lead to various novel physical property materials in past. Thus, we are fully utilizing high-pressure conditions for the materials exploration to discover interesting advanced high-pressure materials such as new high Tc superconductors, magnetic materials, dielectric materials, multiferroic materials, etc. In particular, perovskite transition-metal oxides and related materials are one of the most important targets. In the symposium, I will report our recent results on i) room-temperature ferromagnet system of $\text{Sr}_8\text{ARe}_3\text{Cu}_4\text{O}_{24}$ ($\text{A} : \text{Sr, Ca}$) with an ordered perovskite structure, ii) new bulk multiferroic (magnetic ferroelectric) and ferroelectric materials with the composition of BiMO_3 , PbMO_3 , and $\text{Bi}_4\text{M}_3\text{O}_{12}$ ($\text{M} : \text{transition metal}$), iii) manganate perovskite system of RMnO_3 ($\text{R} : \text{Ho, Er, Tm, Yb, Lu}$), etc. all of which can be prepared only under high pressure. Their high-pressure synthesis and structural and physical properties will be discussed thoroughly in the symposium

Keywords: high-pressure synthesis, perovskite structure, transition-metal oxides

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Synthesis and characterization of metal nitrides

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The interest in the synthesis of the new materials has been always driven by the applications relevant to the technology and fundamental science. Transition metal carbides and nitrides form refractory high-strength high-hardness materials. Recent discovery of platinum nitride (PtN_2) showed the possibility of synthesis of the novel materials at high pressures (e.g. above 50 GPa) and temperatures and their recovery to the ambient conditions in the diamond anvil cell. Here, we present several novel transition and noble metal nitrides including IrN_2 and OsN_2 synthesized at extreme conditions having exceptionally high bulk moduli. Using synchrotron x-ray radiation, Raman spectroscopy, electron microprobe analysis and *ab initio* calculations we characterize the new materials and compare them