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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,  $\text{NaAlH}_4$  and the corresponding salts ( $\text{XCl}_3$  with  $\text{X} = \text{Pr, Nd}$ ) were ball-milled for several hours. The evaluation of the products show the formation of  $\text{NaCl}$  and  $\text{Al}$  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  $120^\circ\text{C}$  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.  $\text{NdAl}_3$  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

## MS.46.5

*Acta Cryst.* (2008). A64, C84

### 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  $\text{H}_2$  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  $\text{H}_2$  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  $\text{D}_2$  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  $\text{H}_2$  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

## MS.47.1

*Acta Cryst.* (2008). A64, C84

### 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,  $\text{MgB}_2$  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  $\text{BiMO}_3$ ,  $\text{PbMO}_3$ , and  $\text{Bi}_4\text{M}_3\text{O}_{12}$  ( $\text{M}: \text{transition metal}$ ), iii) manganate perovskite system of  $\text{RMnO}_3$  ( $\text{R}: \text{Ho, Er, Tm, Yb, Lu}$ ), 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

## MS.47.2

*Acta Cryst.* (2008). A64, C84–85

### 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 ( $\text{PtN}_2$ ) 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  $\text{IrN}_2$  and  $\text{OsN}_2$  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