

Muelheim, Nordrhein-Westfalen, 45470, Germany, E-mail : weidenthaler@mpi-muelheim.mpg.de

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, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$

Jae-Hyuk Her<sup>1,2</sup>, Yun Liu<sup>1,2</sup>, Craig M Brown<sup>1</sup>, Dan A Neumann<sup>1</sup>, Steven S Kaye<sup>3</sup>, Jeffrey R Long<sup>3</sup>

<sup>1</sup>National Institute of Standard and Technology, NIST Center for Neutron Research, 100 Bureau Drive, Stop 6102, Gaithersburg, MD, 20899-6102, USA, <sup>2</sup>Department of Materials Science and Engineering, Univ. of Maryland, College Park, MD 20742, USA, <sup>3</sup>Department of Chemistry, Univ. of California, Berkeley, CA 94720, USA, E-mail : jaehyuk.her@nist.gov

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

Eiji Takayama-Muromachi

National Institute for Materials Science, MANA, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan, E-mail : muromachi.eiji@nims.go.jp

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

Eugene Gregoryanz

CSEC, U. of Edinburgh, JCMB buildings, Mayfield Rd., Edinburgh, Scotland, EH9 3JZ, UK, E-mail : e.gregoryanz@ed.ac.uk

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

with other known transition and noble metal nitrides.

Keywords: high pressure, synthesis, novel materials

### MS.47.3

*Acta Cryst.* (2008). A64, C85

#### High pressure synthesis of nanocrystalline superhard materials

Leonid S. Dubrovinsky

Bayerisches Geoinstitut, University of Bayreuth, Universitaetstr. 30, Bayreuth, D, 95440, Germany, E-mail : Leonid.Dubrovinsky@uni-bayreuth.de

The exceptional physical properties of diamond, cBN, and other superhard materials make them not only valuable gems but also important materials in a wide variety of industries where their extreme hardness, toughness, high refractive index, transparency over a broad spectral range, and high thermal conductivity are exploited. Diamond-like carbon (DLC) nanocrystalline films, polycrystalline cubic diamond and cBN have been attracting rapidly increasing interest that focuses on the design of optimum materials by reducing grain dimensions and on how new useful properties could be achieved. We will discuss fundamental issues of high-pressure, high-temperature synthesis and characterization of advanced superhard nano-materials. The new fields of their application will be also considered. Special emphasis will be given to the novel phases, such as nanodiamond, nano-cBN, diamond-like phases in the B – C – N system, spinel nitrides, oxides, and carbides.

Keywords: high-pressure synthesis, nanophase systems, novel structures

### MS.47.4

*Acta Cryst.* (2008). A64, C85

#### Pressure-induced over-hydration of zeolites: New insights from the elastic behavior of gismondine

Simona Quartieri<sup>1</sup>, Silvia Ori<sup>2</sup>, Giovanna Vezzalini<sup>2</sup>

<sup>1</sup>University of Messina, Dipartimento di Scienze della Terra, Salita Sperone 31, Messina S. Agata, Italy, 98166, Italy, <sup>2</sup>University of Modena and Reggio Emilia, Dipartimento di Scienze della Terra, Via S. Eufemia 19, 41100 Modena, Italy, E-mail: simona.quartieri@unimore.it

High-pressure (HP) structural studies on zeolites compressed in aqueous media have recently attracted great interest on the pressure-induced hydration (PIH) phenomenon - characterized by the penetration of additional water molecules into the zeolite channels - which can in principle modify the zeolite properties, opening possible new scenarios for their industrial applications. This paper reports the results of an in-situ HP synchrotron powder diffraction study performed on the natural zeolite gismondine from Pamb to 7.9 GPa, using methanol:ethanol: water (16:3:1) mixture (m.e.w.) as penetrating P-transmitting medium. The P-induced deformation mode consists in a slight distortion of the double crankshaft chains forming gismondine framework, and in the deformation of the 8-membered rings delimiting the channel apertures, which become more elliptic. From 0.6 GPa, the water content is slightly higher than the initial one, as a result of a moderate over-hydration. Moreover, at about 2 GPa, a significant water molecule system re-arrangement occurs, characterized by an ordering of part of the water molecules from four partially occupied sites to only two fully occupied ones. PIH, but not the water ordering, is substantially irreversible upon

pressure release. At about 3 GPa a phase transition to triclinic symmetry is observed. The comparison of the cell volume reductions and of the bulk moduli of gismondine compressed in m.e.w. and in silicone oil reveals that this is the unique zeolite with a higher compressibility in penetrating vs. non-penetrating P-transmitting media. This is ascribed to the re-organization of the water molecule system upon compression in m.e.w., which leaves a larger free volume inside the pores with respect to the phase compressed in silicone oil.

Keywords: high-pressure-induced over-hydration, high-pressure phase transition, zeolites-microporous materials

### MS.47.5

*Acta Cryst.* (2008). A64, C85

#### Pressure induced transition in nano-TiO<sub>2</sub>: An X-ray absorption spectroscopy study

Jean-Paul Itie<sup>1</sup>, Anne-Marie Flank<sup>1</sup>, Pierre Lagarde<sup>1</sup>, Alain Polian<sup>2</sup>, Giovanni R Hearne<sup>3</sup>

<sup>1</sup>Synchrotron SOLEIL, L'Orme des merisiers, St Aubin, BP48, Gif-sur-Yvette cedex, idf, 91192, France, <sup>2</sup>Physique des Milieux Denses, IMPMC, CNRS, Universite P.et M. Curie-Paris 6, 140 rue de Lourmel 75015 Paris France, <sup>3</sup>School of Physics & DST-NRF CoE in Strong Materials, WITS University, Johannesburg, South Africa, E-mail : jean-paul.itie@synchrotron-soleil.fr

The novel phenomenon of grain-size dependent pressure induced amorphisation (PIA) in TiO<sub>2</sub> nano-materials has been evidenced by several experiments in recent years. Until now, there is no experimental evidence of the length scale of disorder of the amorphous structures nor is there a clear picture, specifically in the case of pressure amorphised anatase-TiO<sub>2</sub> starting material. The open questions of the structural details of the high density amorphous (HDA) phase have been addressed in an x-ray absorption spectroscopy (XAS) pressure study at the Ti K-edge. The local environment of the cation, to within a few nearest neighbour shells, has been monitored up to ~30 GPa where the HDA phase is stabilised. The XAS investigations of this study suggest that a precursor ordered structural phase is observed before amorphisation, the nature of which depends on the experimental conditions. A new structure is stabilized in all cases of samples decompressed from the HDA phase to ambient conditions, characterised by five-fold coordinated Ti. These conceptual pictures are derived from both the EXAFS and the pre-edge parts of the absorption spectra.

Keywords: absorption spectroscopy, nanocrystals, high pressure phases

### MS.48.1

*Acta Cryst.* (2008). A64, C85-86

#### Quantitative electron and X-ray diffraction study of charge density in complex oxides

Yimei Zhu

Brookhaven National Laboratory, Condensed Matter Physics and Materials Science, Building 480, Upton, NY, 11973, USA, E-mail : zhu@bnl.gov

We report our studies on electronic structure and charge density distribution of complex oxides using quantitative electron diffraction, x-ray diffraction and density functional theory (DFT) calculations. The electron diffraction was based on the unique diffraction-imaging