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Acta Cryst. (2011) A67, C247**300 Bar In-situ Gas Pressure Cell for Powder Diffractometers**

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A new in-situ cell has been designed and constructed to simulate the temperature, pressure and chemical conditions present in deep saline aquifers. The cell has been built to study reactions at the CO₂-brine-solid interfaces produced during injection of supercritical CO₂ (sc-CO₂) for storage and sequestration purposes. Much of the data relating to CO₂ storage relates to oil and gas wells. However, by far the largest potential reservoirs are deep saline aquifers where the chemistry has little in common with oil wells. Little experimental data exists on the behavior of various rocks and engineering materials under these conditions, particularly with injection of impure CO₂ streams, and some of the existing data give significant cause for concern.

The cell has been designed for both reflection and transmission geometries so may be used both in laboratory and synchrotron environments. Although sc-CO₂/water often reacts slowly under equilibrium, concerns have been raised about impurities such as SO₂ and H₂S that will inevitably be present in industrial streams. These gases can react rapidly, so the slower laboratory and more rapid synchrotron measurements are highly complementary. Flow-through experiments may also be possible but haven't been specifically targeted.

The cell has maximum working conditions of 300 bar pressure and 300 °C in pH3 brine conditions. These conditions are extremely demanding for any metals, sealing and window materials, and the restrictions imposed by the ASME Pressure Vessel and Boiler Code [1] and Process Piping Code [2] posed additional challenges. The materials certification requirements in the ASME code forced us into using structural grade beryllium windows as in our first generation cell [3]. Beryllium is highly susceptible to chloride corrosion so a thin coating of tantalum is used to protect the windows under these conditions. Requirements of the pressure vessel certification process meant the cell was successfully tested hydrostatically to 450 bar pressure before delivery.

Some of the theoretical and practical considerations for the design and construction of the cell will be described. Although the cell may be used with a laboratory diffractometer, the silver X-ray tube source and high-energy optimized PSD detector needed to gain sufficient penetration and signal are not standard components. Such a cell needs to be operated as part of an overall 'system' and is of limited use in isolation.

[1] American Society of Mechanical Engineers, *Boiler and Pressure Vessel Code* **2010**, ASME, New York. [2] American Society of Mechanical Engineers, *ASME B31.3 Process Piping* **2010**, ASME, New York. [3] P.S. Whitfield, A.V. Nawaby, B. Blak, J. Ross, *Journal of Applied Crystallography* **2008**, *41*, 350-355.

Keywords: powder diffraction, gas, pressure

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Acta Cryst. (2011) A67, C247**A structural phase transition in the R₃Cu₄Sn₄ compounds (R=Ho, Er and Tm)**

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The ternary intermetallic system R₃T₄X₄ (where R = rare earth; T = Mn, Cu, Ag, Au, Pd; X = Si, Ge, Sn) comprises an extensive series of isostructural compounds that crystallize in the orthorhombic Gd₃Cu₄Ge₄-type structure (space group *Immm*, #71) [1]. The exceptions to this generic orthorhombic crystallography are Tm₃Cu₄Sn₄ and Lu₃Cu₄Sn₄ which have a monoclinic structure (space group *C12/m1*, #12) at room temperature [2].

In the orthorhombic phase the R atoms occupy two crystallographically distinct sites [3] and these compounds have attracted interest due to the general observation of independent magnetic ordering of these two R sublattices [1].

The present work reveals that a **structural phase transition occurs** in Er₃Cu₄Sn₄ and Ho₃Cu₄Sn₄ from orthorhombic *Immm* to monoclinic *I12/m1* upon cooling, at 262(2) K and 62(2) K respectively. We also found a structural phase transition at 458(2) K from **monoclinic** *C12/m1* to orthorhombic *Immm* in Tm₃Cu₄Sn₄ upon heating.

The results show a linear behaviour of the crystallographic transition temperatures with the ionic radii of the R³⁺ ions, and predict no transition for the Dy₃Cu₄Sn₄ compound, in accord with our measurements carried out at low temperatures for this compound.

Here, we present complete structural information from high resolution synchrotron X-ray powder diffraction studies of these R₃Cu₄Sn₄ compounds.

[1] D.H. Ryan, J.M. Cadogan, C. Voyer, M. Napolitano, P. Riani, L.M.D. Cranswick, *Mod. Phys. Lett. B* **2010**, *24*, 1-28. [2] F. Thirion, J. Steinmetz B. Malaman, *Mat. Res. Bull.* **1983**, *18*, 1537-42. [3] W. Rieger, *Monatsch. Chem.* **1970**, *101*, 449-62.

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Acta Cryst. (2011) A67, C247-C248**Behaviour of actinide pyrophosphates AnP₂O₇ at high temperatures: An=Th,U,Np,Pu**

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Actinide-bearing phosphate compounds can be encountered in mineralogy [1], biochemistry [2] or issued from anthropogenic activities like nuclear fuel reprocessing. They have also been envisioned and investigated as potential host for actinide waste disposal. Because of their numerous oxidation states (e.g. III to VII for neptunium) and corresponding ionic radii, actinides can form various types of phosphate compounds [3], [4]. In the present studies we focussed on the pyrophosphates family of general formula -AnP₂O₇- in which actinides are tetravalent. Pyrophosphates have attracted a lot of interest over the last decade [5] because they exhibit unusual high temperature properties such as negative thermal expansion above a certain temperature. In the present work we have investigated the structural behaviour of four

actinide-bearing pyrophosphates and found that all of them exhibit this unusual high temperature behaviour above 673K. Besides we also found that their room temperature structure is not cubic as previously reported [6] but triclinic (distorted cubic) and transform into a cubic form around 150°C. The phase transition has been characterized by various experimental techniques, X-ray diffraction, solid-state NMR and Raman spectroscopy. The room temperature structure has been determined by from synchrotron radiation data obtained at the ESRF. Our presentation will report the experimental results and discussed the structural aspect related with the contraction of the materials at high temperatures.

[1] *Reviews in Mineralogy and Geochemistry* 48, Phosphates, ISSN 1529-6466, [2] M.P. Neu, H. Boukhalfa, M.L. Merroun, M.R.S. Bulletin **2010**, 35, 11. [3] R. Jardin, C.C. Pavel, P-E. Raison, D. Bouëxière, H. Santa-Cruz, R.J.M. Konings, K. Popa, *J. Nucl. Mat.* **2008**, 378, 167–171. [4] K. Popa, G. Wallez, P.E. Raison, D. Bregiroux, R.J.M. Konings, *Inorg. Chem.* **2010**, 49, 6904-6908. [5] G.W. Stinton, M. Hampson, J.S.O. Evans, *Inorg. Chem.* **2006**, 45, 4352. [6] C.E. Bamberger, R.G. Haire, H.E. Hellwege, G.M. Begun. *J. Less Common Met.* **1984** 97, 349.

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Crystal Structure and phase transitions of mechanoactivated manganese oxides

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One of the features of the Mn-O system is the formation therein of two Mn₂O₄ spinel-type polymorphs: γ -Mn₂O₄ with a spinel structure (sp.gr. *Fd3m*) and β -Mn₂O₄ with a hausmannite structure (sp.gr. *I4/amd*) often considered as a tetragonally distorted spinel with lattice parameters $a^* = \sqrt{2} a, < c (c/a^* > 1)$. The tetragonal distortion of the spinel lattice is due to the cooperative Jahn-Teller effect, and is caused by Mn(III) ions on octahedral sites. Transformation between the two structures is observed both under equilibrium non-ambient conditions (at 1172°C in air) and on quenching the oxide from a high temperature state to room temperature where only a hausmannite structure exists. In this work effects of mechanical activation on the crystal structure and phase transitions of the treated manganese oxides were studied by high-temperature X-ray diffraction.

Highly activated manganese oxides (MnO₂, Mn₂O₃, Mn₃O₄, and MnO) were prepared by high-energy ball milling ($g>60$). The as-prepared mechanically activated manganese oxides were characterized as single-phased, nanoscaled or ultra-fine-grained compounds.

Ball milling gave rise to a direct phase transition from α -Mn₂O₃ to γ -Mn₂O₄ omitting β -Mn₂O₄ phase during heating. This result was obtained both for the as-treated nanoscaled α -Mn₂O₃ oxide and for the coarse-grained powder after multiple thermal recycling. The same effects were observed upon thermal study of the other activated manganese oxides. A significant increasing in the temperature of the phase transition from Mn₂O₃ to Mn₃O₄ during heating and an easier reversibility of the Mn₃O₄ to Mn₂O₃ phase transition upon cooling were also detected. It was proposed structural defects due to the mechanical activation are responsible for the anomaly in phase transition behaviour of mechanoactivated manganese oxides. Therefore the structure and microstructure of the phases involved were refined depending on treatment conditions and temperature.

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Hybrid instrument for in situ studies at the ESS

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The decision to build the European Spallation Source (ESS) came in the spring of 2009. The ESS will be built in Lund, Sweden and become the most powerful neutron source in the world. The ESS will give unprecedented possibilities for neutron scattering in crystallography and materials science. Investigations of materials at multiple length scales are getting increasingly important for understanding and improving materials performance such as hydrogen storage, solid oxide fuel cells and lithium ion batteries.

A new concept for a neutron scattering instrument will be presented. The new idea combines powder neutron diffraction (PND), small angle neutron scattering (SANS), and neutron imaging (NI) in the same instrument. The PND potentially allows extraction of pair distribution functions for looking at amorphous systems. By combining these techniques it will be possible to look at length scales 0.01-5 nm using diffraction, 1-1000 nm using SANS, and 0.01-100 mm using NI. In addition to the different techniques a high time resolution is envisioned to study processes at the subsecond level. In this way it is possible to study materials *in situ* or *in operandi*.

Through the presentation it is intended to start discussions with the potential user community of the suggested hybrid instrument. The ESS is soon to determine the instrument suite which will be built in the first round. Since this instrument presents new concept there is no existing user community. The IUCr is therefore a great opportunity for engaging with the potential users.

Keywords: neutron scattering, materials, in situ

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Negative thermal expansion in trioxane silica sodalite (TRSS)

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The thermal dehydration and template burning process of a silica sodalite (SS), synthesized in the presence of boric acid and trioxane (TR), Na_{0.15}[B_{0.07}Si_{11.93}O₂₄]-1.8TR, were studied *in situ* by synchrotron powder diffraction up to 900°C. Time-resolved diffraction data were collected at the GILDA beamline at ESRF (Grenoble). Thermal analyses (TG, DTA and DTG) of the as-synthesized samples were carried out in the same temperature range under a constant flux of air (heating rate 5°C/min).

The cell volume of TRSS does not change remarkably until the expulsion of the template, which occurs above 380°C, as inferred by TG analysis weight loss and by the structure refinement of trioxane molecule occupancy. When trioxane molecule decomposition begins, volume expansion becomes negative. This result is unusual for sodalite type materials which typically show positive thermal expansion [1-3]. However, in all these studies the extraframework content is given by cations or anions (such as Cl⁻, F⁻) which cannot be expelled during heat treatment. In our case, extraframework content is represented by organic molecules which are expelled upon heating. A similar result was observed only in a silica sodalite synthesized in the presence of ethylene glycol [4]. These results suggest that when the organic molecules are neutral complex and only act as spacer, a contraction of