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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