

## Poster Sessions

The results of *in situ*, synchrotron X-ray powder diffraction experiments conducted during the (i) the synthesis and (ii) the dehydration of  $\text{Na}^+/\text{H}_3\text{O}^+$  and  $\text{K}^+/\text{H}_3\text{O}^+$  jarosites will be presented. These time-resolved studies provide information regarding the kinetics of formation over temperatures ranging from 80°C to 120°C and also show the occurrence of cation exchange on the A site with time. The synthesis reactions show that samples can be prepared in which the iron-site vacancies are ordered. The ordering is accompanied by a lowering of symmetry, from rhombohedral, space group  $R\bar{3}m$ , to monoclinic,  $C2/m$ . This has implications for the variability of magnetic properties reported for synthetic iron-deficient jarosites.

**Keywords:** jarosite, in situ, synchrotron

### MS05.P02

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#### Crystal structure and magnetic transition in $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{1-y}\text{Ge}_y$ magnetocaloric compounds

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Magnetic refrigeration based on the magnetocaloric effect (MCE) is becoming an alternative technology to replace the conventional gas-compression refrigerators. The compounds of the  $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{1-y}\text{Ge}_y$  system exhibit a reversible giant magnetic-entropy change, adjustable Curie temperature and hence make this material system an excellent candidate for working material in magnetic refrigeration.

Structure and magnetic properties of  $\text{Mn}_{2-x}\text{Fe}_x\text{P}_{1-y}\text{Ge}_y$  compounds as a function of temperature, and applied magnetic field were investigated using neutron powder diffraction. It noted that temperature and magnetic field can induce the first order phase transition between the paramagnetic phase and ferromagnetic phase in the materials. The paramagnetic and ferromagnetic phases have two very distinct crystal structures and the magnetic-phase transition is accompanied by structural transition. In addition, the magnetic-entropy changes as a function of magnetic field or temperature being directly controlled by the phase fraction of this first-order transition. We also found that the crystallites below a threshold size inhibit the paramagnetic to ferromagnetic transformation.

**Keywords:** neutron\_diffraction, magnetic\_refrigerant, crystallography

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#### In Situ Energy-Dispersive Diffraction Studies of Reaction Layers in Inert Anodes

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Many important light metals - including aluminium, magnesium and titanium - can be produced via electrowinning involving the use of carbon anodes in the reduction of solid metal oxides in a molten salt bath (for example, cryolite,  $\text{Na}_3\text{AlF}_6$  or calcium chloride,  $\text{CaCl}_2$ ) operating at  $\sim 1000^\circ\text{C}$ . The carbon anodes can contaminate the light metal product and are consumed at a rapid rate, necessitating frequent replacement and producing carbon dioxide emissions, all of which affects cell stability and reduces cell efficiency.

Inert anodes are a potential replacement for carbon anodes as they are not consumed and evolve only pure oxygen from the melt. As well as reducing costs and greenhouse gas emissions, the inert anode provides greater cell stability and avoids carbon contamination of the product.

*Ex situ* studies suggest that passivating layers form on the inert anode surface upon immersion in the molten bath and wear away during cell operation. These layers are thought to be the key to electrode longevity as they protect the anode from the molten bath. Fundamental study of these layers *in situ* in operating cells is imperative in understanding the mechanism of their formation and wear, and hence, to developing genuinely breakthrough inert anode technology.

To this end, we have developed an experimental facility and analysis methodologies in order to study layer formation in operational electrochemical cells. The facility and methodologies may also be applied to other systems where time-resolved *in situ* measurements of materials in challenging environments are important.

An *in situ* energy-dispersive diffraction study of operational electrochemical cells to observe passivation layers formation on model inert anodes was conducted on beamline I12 (JEEP) at the Diamond Light Source. The diffraction data has been quantitatively analysed by the Rietveld method yielding layer thickness as a function of time, and a kinetics analysis of these results shows that the layer growth is diffusion controlled with a decreasing nucleation rate.

**Keywords:** X-ray diffraction, in situ, electrochemistry

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#### Crystal and magnetic structures of inorganic-organic frameworks using powder diffraction

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The fascinating structures and properties of inorganic-organic hybrid frameworks have made them the focus of extensive study, with much of the focus placed on the nanoporous metal-organic frameworks [1], [2]. Recently denser frameworks with extended inorganic (e.g. metal-oxygen-metal) connectivity have become of increasing interest [1], [3]. These compounds exhibit electronic and magnetic properties more commonly found in purely inorganic compounds. The structure-directing effect of the organic ligands on the framework, however, enable them to adopt unusual structures with unique and often low dimensional properties. The vast majority of structural studies of framework materials are performed using single crystal diffraction but, using a combination of neutron and synchrotron X-ray sources, powder diffraction can be used to examine the details of these architectures with greater precision. Neutron diffraction also allows the magnetic structure of frameworks to be examined in detail, revealing more complex behaviour than often found in purely inorganic compounds.

In this work we present two structural studies of hybrid frameworks with extensive inorganic connectivity, which have been explored using a combination of powder and single crystal diffraction. In the

first of these we present a new divalent Mn succinate framework,  $\text{Mn}(\text{C}_4\text{H}_4\text{O}_4)$ , which undergoes several magnetic phase transitions at low temperature. This compound contains two well separated  $\text{MnO}_6$  octahedral sheets with very different connectivity creating two significantly different and well separated magnetic planes. Neutron powder diffraction has been used to examine the magnetic structure of these planes and this will be presented alongside the important role  $\text{Mn}^{2+}$  plays in stabilising this unusual structure.

The detailed structures of the transition metal gallates will also be explored. In this fascinating family Fe is found in the trivalent form while all other frameworks contain divalent cations. Despite this, however, initial single crystal structural studies did not indicate any significant differences in the structures of these materials. Here we present a subsequent, more precise, study of these compounds using neutron and synchrotron X-ray diffraction. The differences caused by the presence of di- and trivalent cations and the effect this has on the positions and occupancies of the hydrogens in this structure is described. We also explore the magnetic structure adopted, at low temperatures, by the one dimensional  $\text{CoO}_6$  octahedral chains in Co gallate.

[1] C.N.R. Rao, A.K. Cheetham, A. Thirumurugan, *Journal of Physics Condensed Matter* **2008**, 20, 083202. [2] J.R. Long, O.M. Yaghi, *Chemical Society Reviews* **2009**, 38, 1213. [3] M. Kurmoo, *Chemical Society Reviews* **2009**, 38, 1353.

**Keywords:** neutron, powder diffraction, magnetic structure

## MS05.P05

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**Temperature and pressure evolution of the crystal structure of  $A_x(\text{Fe}_{1-y}\text{Se})_2$  ( $A = \text{Cs}, \text{Rb}, \text{K}$ ) studied by synchrotron X-ray diffraction.**

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Temperature ( $\text{Cs}_x(\text{Fe}_{1-y}\text{Se})_2$ ) and pressure evolution of crystal structures ( $\text{Cs}_x(\text{Fe}_{1-y}\text{Se})_2$ ,  $\text{Rb}_x(\text{Fe}_{1-y}\text{Se})_2$  and  $\text{K}_x(\text{Fe}_{1-y}\text{Se})_2$ ) was studied using synchrotron powder diffraction. The structure of  $\text{Cs}_{0.83}(\text{Fe}_{0.86}\text{Se})_2$  possesses phase transition on heating related to disorder of iron vacancies in the FeSe layer, as we have shown before [1] and in agreement with other reports [2]. At variance with results reported in [2, 3], we found the transition to be of the first order as evidenced by hysteresis in lattice properties and also agrees with differential scanning calorimetry [1]. At the same time, we have noticed an irreversibility of the temperature dependence of the lattice dimensions and Bragg intensities. We tentatively relate the irreversibility to a mobility of intercalating alkali ions; such a mobility may seriously affect apparent temperature evolution of the crystal structure.

Diffraction experiments as a function of pressure allowed to recover equation of states and, for the first time, provide with experimental estimates of the bulk moduli. We have also seen that the Bragg reflections indicative of vacancies ordering in the FeSe layer do not disappear up to  $\sim 120$  kbar. Albeit refinement of crystal structure suffers from limited quality of diffraction data collected in diamond anvil cells, no clear anomaly for  $\text{Cs}_{0.83}(\text{Fe}_{1-y}\text{Se})_2$ ,  $\text{Rb}_{0.85}(\text{Fe}_{1-y}\text{Se})_2$  and  $\text{K}_{0.8}(\text{Fe}_{1-y}\text{Se})_2$  ( $y \sim 0.14$ ) was observed around 80 kbar, where transport experiments indicate an offset of superconductivity. Albeit definitive

answer can only be obtained from diffraction experiment at high pressure and very low temperatures, our data indicates that ordering of vacancies in the FeSe layer may be present in both superconducting and non superconducting states.

**Keywords:** superconductor, synchrotron X-ray diffraction, Pressure

## MS05.P06

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**Neutron diffraction on functional materials using special sample environments**

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The high-resolution neutron powder diffractometer SPODI (FRM II / Garching n. Munich) offers a range of possibilities for in-situ materials characterisation under special sample environmental conditions.

Bulk samples of ferroelectric ceramics were investigated under the influence of high electric fields up to 7 kV/mm (35 kV) in a SF6 gas atmosphere to establish correlations between the macroscopic poling behaviour and corresponding structural changes. Here we report investigations on lanthanum doped lead zirconate titanate (PLZT) with compositions around the morphotropic phase boundary [1] and also on a bismuth sodium titanate based system (BNT-BT-KNN) [2]. The neutron diffraction studies are accompanied by X-ray and synchrotron diffraction as well as transmission electron microscopy. In the system BNT-BT-KNN at composition 92-6-2, the field induced macroscopic strain can be explained by a phase transformation during the poling process. At 6 kV/mm the transition to a rhombohedral phase was identified by corresponding superlattice reflections, arising from a superstructure in the tilting angles of the oxygen octahedra around Ti/Zr atoms. The data were analysed by Rietveld refinement. In lanthanum doped PZT samples with different Ti/Zr compositions, systematic changes in the response to the electric field were observed for different compositions across the morphotropic phase boundary: different changes of lattice distortions and anisotropic displacement parameters of the lead cations were found.

Other in-situ neutron diffraction studies on SPODI comprise e.g. the structural changes in lithium-ion batteries during charging/discharging which were investigated in-operando by a potentiostat or deuterium charging of hydrogen storage materials with  $\text{D}_2$  pressures up to 100 bar in cooperation with the Joint Research Centre of the European Commission in Petten [3]. The anisotropy of material reactions under mechanical load is studied with a rotatable load frame, allowing the selection of any direction of the applied field with respect to the diffraction plane.

[1] Hinterstein et al, *Z. Krist.* **2011**, 226, 162. [2] Hinterstein, et al, *J. Appl. Cryst.* **2010**, 43, 1314-1321. [3] F. Dolci, et al, *Int. J. Hydr. Energy*, **2010** 35(11), 5448-5453.

**Keywords:** neutron diffraction, ferroelectrics, powder diffraction