

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

Acta Cryst. (2011) A67, C238

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

MS05.P03

Acta Cryst. (2011) A67, C238

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, Na_3AlF_6 or calcium chloride, 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

MS05.P04

Acta Cryst. (2011) A67, C238-C239

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