

The nano-size iron oxide,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, lithiated chemically was subjected to neutron scattering studies for crystal structure analysis by Rietveld method and for local structure analysis by total diffraction technique. The lithium intercalation of the nano-size  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> proceeded by a biphasic reaction through the defect spinel and the disordered rock-salt phases. Pair distribution functions calculated from the total scattering data indicated a correlation of Li-O with a distance of 2.36 Å, which is much longer than the bond distance in ionic crystals. Lithiation mechanism of the nano-size materials will be discussed based on the bulk and local structure changes clarified by these neutron scattering techniques.

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Keywords: nanocrystals, iron oxides, neutron scattering

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#### Free oxygen ions in nanoporous material 12CaO·7Al<sub>2</sub>O<sub>3</sub> and cage deformation at high temperature

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There has been great interest for a decade in the nanoporous material 12CaO·7Al<sub>2</sub>O<sub>3</sub> (C12A7) because of variety of fascinating characteristics the material exhibits, including high ionic conductivity of oxygen ions at high temperature. The characteristics are mostly due to its unique structure. The framework structure of C12A7 in a unit cell can be represented as [Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup> which consists of twelve cages with inner free space of ~ 4 Å in diameter. Two remaining oxygen ions, so called free oxygen ions, are believed to be captured in the inner space of two cages out of the twelve cages. The free oxygen ions are considered to play an important role in the oxide ion conduction. In order to obtain precise structural information, including the position of the free oxygen ions, neutron powder diffraction studies were carried out over a wide temperature range, 50 K - 700 K. The structure analyses clearly indicated that the free oxygen ion is located inside the cage and the position is displaced from the S<sub>4</sub> axis running through the center of the cage. It was also confirmed that the presence of the free oxygen ion in the cage induces a deformation of the cage. Calcium ions at the top and the bottom of the cage are shifted toward the center of the cage when the free oxygen ion is present in the cage. The framework structure was found to be further deformed as the temperature is elevated. The deformation involves; lengthening of aluminum-oxygen bond lengths; shortening of a distance between an oxygen ion in the cage wall and the free oxygen ion. These variations may enhance the oxygen ion migration at high temperature. A complete description of the deformation at high temperature and a possible mechanism of the oxygen ion migration will be presented.

Keywords: crystal structure-physical property relationships, ionic conductors, neutron diffraction

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#### Residual stress investigation of dissimilar overlap-friction stir welds made from Al and steel

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One of the main research topics at the GKSS Research Centre is the investigation and further development of friction stir welding techniques. In this context dissimilar overlap joints of sheets made from aluminum and steel were produced by friction stir welding at GKSS. A set of four different specimens was produced with different welding and tool speeds. Aluminum alloy AA5754-H22 and dual phase steel alloy DP600 were used. The aluminum and steel sheets were 1.5 mm thick and the stirring zone was 12 mm wide. The residual stress distribution in these specimens was investigated at the high energy materials science synchrotron beamline HARWI II operated by GKSS at the HASYLAB / DESY, Germany. A beam with a photon energy of 100 keV and a size of 2 x 0.2 mm<sup>2</sup>, with the larger beam dimension being parallel to the weld, was used in transmission geometry. A Mar345 detector system was employed to monitor complete Debye-Scherrer rings. The diffraction peak shifts of the Al {311} and Fe {211} lattice planes were used to determine the residual stress in the respective material. Peak positions were determined relatively to the Cu {220} peak of a Cu-powder directly attached to each specimen. This allowed the correction for peak shifts induced by the distortion of the specimens and the resulting change of the sample-to-detector distance. The results for the weld zone show that the stresses in weld direction are close to the yield strength for the steel and about 70% of the yield strength for Al. Furthermore, high welding and tool rotation speeds result in steeper stress gradients in steel and almost symmetric stress profiles in both materials, whereas low welding and tool rotation speeds result in a broader stress profile in steel and asymmetry of the profiles in both materials.

Keywords: friction stir welding, residual stress, high energy synchrotron radiation

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#### Residual stresses associated with laser bending of mild steel plates

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Bending of metal plates with high-energy laser beams presents a flexible materials forming technique where bending results from the establishment of a steep temperature gradient through the material thickness. This inevitably leads to non-uniform thermal expansion/contraction and subsequently residual stresses. Non destructive residual strain mapping with diffraction techniques through the 8mm thickness of a series WA 300 grade structural steel plate samples, focused on the region straddling the centerline of the heating bead location, shows the presence of large residual stress fields. Directly below the laser track the longitudinal strains are tensile and dominant, normal strains compressive and transverse strains slightly tensile.

The magnitudes of the strains decrease outside the width of the laser beam footprint. The first laser pass induces through-thickness strains close to yield, whereafter their magnitudes decrease with increased number of laser beam passes. A comprehensive mapping of the longitudinal stresses as function of the number of laser passes is given.

Keywords: strain scanning, laser bending, residual stress

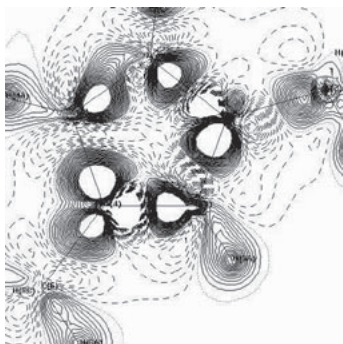
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#### Charge density and *in-situ* studies of ionic and ionothermally prepared materials

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X-ray diffraction is an important technique in structure determination. However zeolites and many of the porous materials we look at are notoriously difficult to grow as large single crystals. With the use of synchrotrons such as the SRS we are able to probe these fascinating structures to obtain not only initial structural models but also high resolution X-ray data sets (figure1). Our group uses stations 9.8 and 16.2 SMX to investigate these materials. We are also using the high energy dispersive beam line of 16.4 to investigate how they crystallise. We are able to produce porous materials with the use of ionic liquids which act as both a template and as a solvent reducing the number of interactions in the vessel making it easier to try and understand the mechanism.



Keywords: ionothermal prepared materials, high Resolution Charge Density, porous materials

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#### Hydrothermal synthesis and structural features of metal phosphates in the presence of amines

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Since the first crystalline compound,  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, was obtained, these compounds have been extensively studied due to the possibility of relating their properties and crystalline structure, and the many potential applications. Initially,  $\gamma$ -Zr(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>)·2H<sub>2</sub>O, was erroneously believed to be a modification of the  $\alpha$ -phase. Advances in the knowledge of the  $\gamma$ -layered structure were fundamental for the interpretation of the topotactic mechanism of formation and development of the chemistry of the  $\gamma$ -derivatives. Although only two crystalline forms of layered titanium phosphates are known,  $\gamma$ -

-Ti(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and  $\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>)·2H<sub>2</sub>O, many derivatives have been reported. Surprisingly, the  $\gamma$ -layered titanium phosphate is less studied than the  $\alpha$ -phase, even though the  $\gamma$ -layers are more rigid, thicker, acidic and amenable to intercalation processes. More than a decade ago, we have reported the mechanism of intercalation of n-alkylamines in  $\gamma$ -titanium phosphate, showing that only 66% of the P-OH groups interact with the amine groups of the guest molecules. Geometrical constraints dictate that compounds with maximum intercalation usually have the empirical formula of  $\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>)·1.3C<sub>n</sub>H<sub>2n+1</sub>NH<sub>2</sub>·H<sub>2</sub>O (with n = 1 to 6), and crystalline phases with lower amine content can also be isolated. The hydrothermal synthesis and the structural characterization of  $\gamma$ -titanium phosphate intercalation compounds have been only recently reported.[1,2]

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Keywords: phosphates, hydrothermal synthesis, amines

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#### Iron incorporated in cubic mesoporous silica: Synthesis, composition and structure

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Ordered mesoporous silica (OMS) grafted with different atoms are interesting new structures with high specific surface, large pore size and uniform pore distribution for potential applications in, for example, catalysis, green chemistry and drug delivery systems. In this work, we report the direct incorporation of iron in OMS, with cubic FDU-1 structure. The structural properties of samples prepared under different conditions were investigated by Small Angle X-ray Scattering (SAXS) and large angle X-ray Diffraction (XRD). The local structure around the iron atoms was analyzed by X-ray absorption spectroscopy (XAS). The composite material is mostly formed by amorphous silica and hematite, with some amount of Fe<sup>2+</sup> in the structure. The morphology, structural and textural properties were analyzed by N<sub>2</sub> adsorption isotherms. The variation of the synthesis pH from 1 to 3 decreased the total surface area. Rutherford Backscattering Spectrometry (RBS) was used to determine the amount of Si, O, Cl and Fe in the samples. The amount of iron inside the silica matrix depended on the preparation method, and an optimized synthesis process has been developed aiming to obtain high iron content (up to 4 wt.%) and low chlorine incorporation.

Keywords: porous materials, SAXS, EXAFS and XANES

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#### Cation exchange mechanism for natural apatite with a simulated Cd-polluted solution TEM-AEM and XPS

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