

P.11.16.7*Acta Cryst.* (2005). A61, C406**Ionic Conduction Path and Disorder in LaGaO₃-based Fast Oxide-ion Conductors**

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We have investigated the nuclear density distributions in LaGaO₃-based perovskites, LaGaO₃ (LG), (La_{0.9}Sr_{0.1})GaO_{3-δ} (LSG), La(Ga_{0.9}Mg_{0.1})O_{3-δ} (LGM), and (La_{0.8}Sr_{0.2})(Ga_{0.8}Mg_{0.15}Co_{0.05})O_{3-δ} (LSGMC), to elucidate the ionic conduction path and disorder of oxide ions at elevated temperatures. Neutron diffraction data were collected in the temperature range from 26 to 1405°C in air, using a diffractometer HERMES installed at JRR-3M in JAERI (Tokai). The data obtained were analyzed by the combination technique of Rietveld analysis (using a computer program RIETAN-2000) and a maximum-entropy method (MEM)-based pattern fitting (using a computer program PRIMA). At ca. 1400°C, the oxide ions were localized near the equilibrium (ideal) positions for LG, while they spread over a wide area around the ideal positions for LSG and LGM. For LSGMC, the conduction path of oxide-ion was observed; the conduction path was not along the straight line between the ideal oxygen positions, but exhibited an arc shape away from the B-site cations (Ga_{0.8}Mg_{0.15}Co_{0.05}) [1]. The difference in nuclear density distribution is presumed to arise from the difference in oxide-ion conductivity of these compounds.

[1] Yashima M., Nomura K., Kageyama H., Miyazaki Y., Chitose N, Adachi K, *Chem. Phys. Lett.*, 2003, **380**, 391.

Keywords: LaGaO₃, oxide-ion conduction path, maximum entropy method

P.11.16.8*Acta Cryst.* (2005). A61, C406**Spin Crossover Iron complexes in 2D and 3D Frameworks**

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A new ligand, trans-4,4'-azo-1,2,4-triazole (atr) was designed and synthesized to construct the possible candidates for spin crossover system. It could be served as a multi-dentate ligand or a good linkage ligand.[1] A series of Fe(II) polymeric compounds in 1D, 2D and 3D frameworks have been successfully synthesized and studied structurally and magnetically. The crystal structures of the ligand and the series of polymeric Fe(II) complexes will be presented. In all the complexes, each ligand atr serves as a bridge between two Fe(II) centers; There are water molecules and NCS ligand around each Fe(II) in the 1-D polymeric compound, [Fe(μ-atr)(NCS)₂(H₂O)₂]; An additional bridge ligand, pyz, is used to form a rectangular 2D framework, [Fe(μ-atr)(μ-pyz)(NCS)₂] 4H₂O. A cationic species with Fe to atr ratio of 1 to 3 is formed in a 3D framework with the perchlorate as the inclusion counter anions, [Fe(μ-atr)₃](ClO₄)₂ 2H₂O, the structure shows a interlock network. The magnetic properties are quite interesting: It is paramagnetic for the 1D system but display spin transitions for both 2D and 3D systems. It exhibits an abrupt spin transition at T_c=225 K for [Fe(μ-atr)(μ-pyz)(NCS)₂] 4H₂O. However, it shows a two-step spin transition for the 3D frameworks [Fe(μ-atr)₃](ClO₄)₂ 2H₂O.

[1] Kahn O., Martinez C.J., *Science*, 1998, **279**, 44.

Keywords: spin crossover, framework structures, magnetic property

P.11.16.9*Acta Cryst.* (2005). A61, C406**“Trigger” Mechanisms of Ultra-Fast Reactions**

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While it is well established that rates of reaction will diverge for chemically homogeneous systems during increased heating [1], most solid state materials synthesis involves inhomogeneous mixtures of discrete particles that limit reaction rates by the need for interparticle diffusion. *In-situ* diffraction is a well established technique for the time-resolved analysis of such reactions. We present recent data that demonstrates the importance of several fundamental “trigger” mechanisms for initiating ultra-fast, self-sustaining reactions. These trigger mechanisms rely on phenomena which provides a discontinuity in the relative diffusivity of key reactants. Important examples of these experimental observations include the α→β transition in titanium (~920°C), which influences the solid-solid combustion reaction (SHS) of several systems (e.g. Ti₃SiC₂ [2] and Ti₅Si₃ [3]), and the solid → liquid state transition of aluminium (~660°C), verified to be the initiating mechanism for other SHS reactions. In addition, the influence of these trigger mechanisms on slower processing techniques (e.g. sintering) can explain why higher order systems may not completely react. By understanding these mechanisms and how they influence reaction dynamics, processing can be optimised. Central to this is the continued development of *in-situ* diffraction.

[1] Lacey A.A., *Proc. R. Soc. Lond. A*, 1992, 145-152. [2] Riley D.P., Kisi E.H., Hansen T.C., Hewat A.W., *J. Am. Cer. Soc.*, 2002, **85**, 2417-2424. [3] Riley D.P., Oliver C.P., Kisi E.H., “*In-situ* Neutron Diffraction of Titanium Silicide, Ti₅Si₃, during Self-Propagating High-Temperature Synthesis (SHS)”, *Accepted Intermetallics* 2005.

Keywords: *in-situ* diffraction, reaction mechanisms, kinetics

P.11.16.10*Acta Cryst.* (2005). A61, C406**Investigations on Metal Alanates using X-ray and Neutron Powder Diffraction**

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We report extensive studies on 2% titanium-doped and un-doped sodium aluminium hydride using neutron powder diffraction data collected at 5K and 303K. This substance is of considerable interest because it has been shown to be promising as a material for effective hydrogen storage due to its high hydrogen weight capacity and low cost. [1] Doping with titanium renders the release of hydrogen reversible and the reaction is accelerated at moderate temperatures and pressures. [2] However, there is considerable argument concerning the precise form taken by the titanium in the doped alanate and there is, at present no definitive evidence for any particular theory. [3] These studies were undertaken with the aim of providing further insight into this question.

X-ray powder diffraction data has been collected on hydrided and dehydrided lithium and sodium aluminium hydrides. Studies on the precise nature of the phases present in these materials will be reported.

[1] Ñiguez J., Yildirim T., Udovic T.J., Sulic M., Jensen C.M., *Phys. Rev. B.*, 2004, **70**, 060101-1. [2] Bogdanovic B., Schwickardi M., *J. Alloys Compd.*, 1997, **253**, 1. [3] Brinks H.W., Jensen C.M., Srinivasan S.S., Hauback B.C., Blanchard D., Murphy K., *J. Alloys Compd.*, 2004, **376**, 215.

Keywords: alanates, metal hydrides, neutron diffraction

P.11.16.11*Acta Cryst.* (2005). A61, C406-C407**Structural Characterization and LIESST Properties of Spin Crossover Complex *trans*-[Fe(abpt)₂(NCS)₂] polymorph D (abpt = 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole)**

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A polymorph D of Complex *trans*-[Fe(abpt)₂(NCS)₂] was synthesized and structurally characterized. It crystallize in a monoclinic space group P2₁/c with cell parameter *a* = 10.803(1), *b* = 15.926(1), *c* = 17.451(2) Å, β = 106.81(1)°, *V* = 2874.1(4) Å³ and *Z*=1

at 293 K. The asymmetric unit contains two unique iron sites (Fe and Fe'); each is located at the crystallographic inversion centers. The main difference in these two molecules is the planarity of the abpt ligand; the dihedral angle between the triazole ring and the uncoordinated pyridine ring is 6.2 and 20.1° for Fe and Fe' complex respectively. The result of temperature-dependent FTIR spectra indicates that Fe undergoes a gradual spin crossover transition in the temperature range of 200 ~ 100 K ($T_c = 145$ K), while the Fe' remains at high spin state in the temperature range studied. This shows a definite correlation between the spin crossover character and the planarity of the ligand in this complex; this applies to the known crystal structures of polymorph A^[1] and B^[2]. The closer to the planar of the ligand abpt is, the easier a spin crossover complex will be. The single crystal diffraction data at 90 K were also studied. Comparing to the structure at 293 K, the Fe-N_{avg} distances change from 2.155(3) to 1.976(3) Å at site Fe and 2.163(2) to 2.181(2) Å at site Fe', it is consistent with the FTIR measurement. Below 50 K, the Fe site can be excited from low spin to high spin state using a green light laser (532 nm), the light induce excited spin state strapping (LIESST) process was monitored by the CN stretching frequency in the range of 1900-2200 cm⁻¹.

- [1] Moliner N., Muñoz M. C., Létard S., Létard J., Solans X., Burriel R., Castro M., Kahn O., Real J. A., *Inorganica Chimica Acta*, 1999, **291**, 278-288.
 [2] Gaspar A. B., Munoz M. C., Moliner N., Ksenofontov V., Levchenko G., Gülich P., Real J. A., *Monatshefte Fur Chemie*, 2003, **134**, 285-294.

Keywords: spin crossover, LIESST, FTIR

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The Crystal Structures of the Iron Carbides

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Various low temperature iron carbides are formed in the reactor during the Sasol Synthol process to produce hydrocarbons. The small particle sizes of the iron carbides prevented complete structure determination in the past. Modern equipment is available to study the crystal structures of the iron carbides. The improved crystal structures can then be used to characterize the commercial catalyst samples.

Hägg carbide (χ -Fe₅C₂) and pseudo hexagonal (ϵ' -Fe_{2.2}C) iron carbide samples have been prepared from spray-dried hematite. The preparations were done in an Anton Paar reaction chamber mounted on an X'Pert Pro diffractometer.

The samples were characterized using SEM, powder X-ray diffraction and room temperature Mössbauer spectroscopy. Structure determination with powder diffraction (SDPD) was used to determine the structures of the iron carbides. Rietveld refinements with X'Pert Plus and GSAS software were done on the powder X-ray diffractograms.

Keywords: iron carbide, powder diffraction, SDPD

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Classification of White Marble Varieties by Monocrystal X-ray Diffraction

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A classification of white marble which was not influenced by human evaluation is of paramount importance for the Spanish marble industry and in particular for the industry of the Spanish area of Macael (Almería). The Macael-marble is characterized by a nice white color linked to interesting mechanical properties for building that have provided to this class of marble to be a very appreciate material used for centuries in a large variety of Spanish and American palaces for example the Alhambra of Granada. Instead of the economical and cultural importance of this material, no instrumental procedures were developed to differentiate and classify the Macael-marbles from others

white marbles characterized by less convenient building properties. As a result of the research collaboration between the "University of Almeria-Servicio de rayos X" and the "Centro Tecnológico Andaluz de la Piedra" (CTAP) a new procedure for marble analysis has been obtained. The method basically consists in determining the cell dimensions of the marbles by monocrystal X-ray diffraction. The analysis and comparison of evaluated marble cell parameters led to a reproducible procedure which provides an easy, fast and economical method to a selective identification and classification of the Macael-marbles and of the white marbles in general.

Keywords: white marble, monocrystal X-ray diffraction, marble classification