

**P.11.16.7***Acta Cryst.* (2005). A61, C406**Ionic Conduction Path and Disorder in LaGaO<sub>3</sub>-based Fast Oxide-ion Conductors**

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We have investigated the nuclear density distributions in LaGaO<sub>3</sub>-based perovskites, LaGaO<sub>3</sub> (LG), (La<sub>0.9</sub>Sr<sub>0.1</sub>)GaO<sub>3-δ</sub> (LSG), La(Ga<sub>0.9</sub>Mg<sub>0.1</sub>)O<sub>3-δ</sub> (LGM), and (La<sub>0.8</sub>Sr<sub>0.2</sub>)(Ga<sub>0.8</sub>Mg<sub>0.15</sub>Co<sub>0.05</sub>)O<sub>3-δ</sub> (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<sub>0.8</sub>Mg<sub>0.15</sub>Co<sub>0.05</sub>) [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:** LaGaO<sub>3</sub>, 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)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]; An additional bridge ligand, pyz, is used to form a rectangular 2D framework, [Fe(μ-atr)(μ-pyz)(NCS)<sub>2</sub>] 4H<sub>2</sub>O. 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)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> 2H<sub>2</sub>O, 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<sub>c</sub>=225 K for [Fe(μ-atr)(μ-pyz)(NCS)<sub>2</sub>] 4H<sub>2</sub>O. However, it shows a two-step spin transition for the 3D frameworks [Fe(μ-atr)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> 2H<sub>2</sub>O.

[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. Ti<sub>3</sub>SiC<sub>2</sub> [2] and Ti<sub>5</sub>Si<sub>3</sub> [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, Ti<sub>5</sub>Si<sub>3</sub>, 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)<sub>2</sub>(NCS)<sub>2</sub>] 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)<sub>2</sub>(NCS)<sub>2</sub>] was synthesized and structurally characterized. It crystallize in a monoclinic space group *P*2<sub>1</sub>/*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) Å<sup>3</sup> and *Z*=1