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Keywords: copper complex, topology, hydrothermal synthesis

MS52.27.4

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Influence of the Substituent in the Crystal Packing of Copper(II)-malonates

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The design of new molecular materials with interesting magnetic properties can be achieved following different approaches. The introduction of a secondary ligand, the combination of metal centres or the modification of the primary ligand can be some of these strategies. In the context of our magneto-structural research with malonato-bridged copper(II) complexes and in order to obtain novel coordination modes that could enhance the magnetic exchange coupling we have studied the influence of the substituted malonate ligand in copper(II) complexes.

Complexes of the form $[\text{Cu}(\text{L}^{\text{I}})(\text{H}_2\text{O})_n]$ and $[\text{Cu}(\text{L}^{\text{II}})_2(\text{H}_2\text{O})_n]$ $[\text{Cu}(\text{H}_2\text{O})_n]$ with L^{I} = malonate, ethylmalonate, methylmalonate and L^{II} = malonate, phenylmalonate, are synthesized. Crystal structures vary from the discrete units of copper(II) malonate compounds [1] to the different conformations of two-dimensional structures of ethylmalonate and methylmalonate. Overall ferromagnetic exchange coupling is found in all of these compounds.

Subtle changes in the nature of the substituent can modify the crystal packing and hence the magnetic properties present in these compounds.

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Keywords: copper coordination compounds, crystal packing, magnetic properties

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Hydrogen Storage in Metal-Organic Frameworks

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Reticular synthesis (logical construction of networks from molecular building blocks) has yielded a new class of crystalline porous materials commonly referred to as metal-organic frameworks (MOFs) in which metal ions and clusters are linked by organic units. The ability to prepare MOFs in high yield and with adjustable pore size, shape and functionality has led to their study as gas sorption materials. We have demonstrated that systematic variation of the organic component in isoreticular metal-organic frameworks (IRMOFs) has a marked effect on their capacities for methane. More recently, we discovered that IRMOFs are also capable of storing significant amounts of H_2 , and inelastic neutron scattering studies of molecular hydrogen adsorbed in IRMOF-1 pointed to the organic unit as one of the important adsorption sites. Thus, there is an acute need to collect and analyze more hydrogen uptake measurements on such materials in order to establish the favorable factors for its storage. Hydrogen adsorption isotherms measured at 77 K show a distinct dependence of uptake on the nature of the link for a set of five MOF materials containing the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster. At 1 atm, the materials sorb between 4.2 and 9.3 molecules of H_2 per formula unit. The results imply a trend in hydrogen capacity with the number of rings in the organic moiety. Additionally, the significant influence of the inorganic unit, namely when open metal sites are present, on hydrogen uptake will be presented.

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Keywords: hydrogen storage, metal-organic frameworks, adsorption

MS53 MATERIALS FOR ENERGY CONVERSION AND STORAGE

Chairpersons: John Irvine, Torbjörn Gustafsson

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Electrochemical Materials – Structure in Action

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There are a number of different examples of how *in situ* X-ray diffraction have been used to study lithium insertion/extraction mechanisms of electrode materials in Li-ion batteries [1,2]. In general, the structural changes during a continuous discharge or charge of the battery are followed, giving information about phase transformations in the material. Few, however, have utilized *in situ* X-ray diffraction during potential steps to get time resolved information of the material's response to, for instance, pulsed charges. With the use of synchrotron radiation with high beam intensity and therefore fast exposure times, new results will be presented for some important cathode materials in Li-ion batteries, for example $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, vanadium-oxide nanotubes and Mo_6S_8 . For this purpose, different instrument geometries and detector systems for transmission mode have been explored in combination with special built sample holders. All the experiments have been carried out at MAXlab, the Swedish synchrotron radiation source but the quality of the result will be discussed in the light of earlier obtained results using "in-house" *in situ* X-ray diffraction.

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Keywords: battery materials, time-resolved scattering studies, synchrotron X-ray diffraction

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PDF and NMR Study of Ordering in the Positive Electrode Material $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$

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The local environments and short-range ordering of $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$, a potential Li-ion battery positive electrode material^{1,2}, were investigated by using a combination of X-ray and neutron diffraction and isotopic substitution, Li MAS NMR spectroscopy and, for the first time, X-ray and neutron Pair Distribution Function (PDF) analysis, associated with Reverse Monte Carlo (RMC) calculations. $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ adopts the LiCoO_2 structure and comprises separate Li layers, transition metal (Ni,Mn) layers and O layers.

NMR experiments and Rietveld refinements showed that there is 10% of Li/Ni site exchange. Neutron PDF analysis revealed considerable local distortions in the layers that are not captured in the LiCoO_2 model. Large clusters were built to investigate cation ordering, by performing RMC calculations. Both NMR and RMC were consistent with a non-random distribution of Ni, Mn and Li cations in the transition metal layers. Constraints from both methods showed the presence of short-range order in the transition metal layers comprising LiMn_6 and LiMn_5Ni clusters combined with Ni and Mn contacts that are consistent with those found in some of the proposed structures based on Li_2MnO_3 -like ordering of the cations.

[1] Ohzuku T., Makimura Y., *Chem. Lett.*, 2001, 744. [2] Lu Z., MacNeil D. D., Dahn J.R., *Electrochem. Solid-State Lett.*, 2001, **4**, A191.

Keywords: lithium batteries, pair distribution function, NMR

MS53.27.3*Acta Cryst.* (2005). A61, C70**Hydrogen Storage in light complex Hydrides – structural studies**Bjørn C. Hauback^a, Hendrik W. Brinks,^a ^a*Institute for Energy Technology, Kjeller, Norway.* E-mail: bjorn.hauback@ifef.no

The most important unsolved problem for the introduction of the Hydrogen Economy is efficient and safe storage of hydrogen. Alanates, compounds based on the AlH_4^- unit, are among the most promising metal hydrides for reversible hydrogen storage. The storage capacity is large, e.g. NaAlH_4 can release 5.6 wt% hydrogen below 200 °C. Work during the last years has revealed that Ti additives improve the kinetics of NaAlH_4 and also make re-hydrogenation possible. In order to improve the understanding of the effect of additives and absorption/desorption processes in general, detailed structural studies are very important.

Crystal structures of MAID_4 , (M=Li, Na, K) Li_3AlD_6 , $\text{Mg}(\text{AlH}_4)_2$ and mixed alanates, like $\text{Na}_2\text{LiAlD}_6$, have been determined from high resolution powder neutron and X-ray diffraction. To understand the nature of additives high-resolution synchrotron X-ray and neutron diffraction experiments have been carried out. NaAlH_4 added with Ti-compounds shows no sign of solid solution of Ti into neither Na nor Al positions. However, samples being cycled indicate the presence of an $\text{Al}_{1-x}\text{Ti}_x$ alloy. In-situ desorption experiments (both synchrotron X-ray and neutron diffraction) have been important for detailed studies of the desorption processes. LiAlD_4 has been shown to decompose completely to LiD, Al and D_2 at 127 °C, releasing 7.9 wt% hydrogen. Addition of VCl_3 by ball milling significantly increases the reaction rate. Recent synchrotron X-ray in-situ experiments will be presented.

Keywords: metal hydrides, powder neutron diffraction, powder X-ray diffraction

MS53.27.4*Acta Cryst.* (2005). A61, C70**Structural Analysis of $\text{La}_2\text{Mo}_2\text{O}_9$ -based fast Oxide-ion Conductors**Philippe Lacorre^a, Gwenaél Corbel^a, Yvon Lalignat^a, François Goutenoire^a, Emmanuelle Suard^b, ^a*Laboratoire des Oxydes et Fluorures, UMR CNRS 6010, Université du Maine, 72085 Le Mans cedex 9, France.* ^b*Institut Laue-Langevin, BP 156, 38042 Grenoble cedex 9, France.* E-mail: philippe.lacorre@univ-lemans.fr

Most substitutes to La or Mo in fast oxide-ion conductor $\text{La}_2\text{Mo}_2\text{O}_9$ [1] stabilise, above a certain content, the high-T partly disordered cubic β -form at room temperature. Their cell volume vary quasi-linearly upon substitution, with a Vegard-type evolution, as for instance in the $\text{La}_2\text{Mo}_{2-x}\text{Cr}_x\text{O}_9$ series [2].

The only known exception to this general trend is the series $\text{La}_2\text{Mo}_{2-x}\text{W}_x\text{O}_9$, which shows first a slow increase, then a clear decrease of the crystal cell parameter upon increasing tungsten content [2]. This is at variance with ionic radii, tungsten being slightly larger than molybdenum. Since tungsten has a stabilizing effect relative to the reducibility of $\text{La}_2\text{Mo}_2\text{O}_9$ [3], we have studied in detail its structural effect on this molybdate using neutron powder diffraction.

The main detected incidence on the oxygen sublattice is a change in site occupations, corresponding to a lowering of tungsten coordination number relative to molybdenum, without much change in individual metal-oxygen distances [2]. A new kind of description of the β - $\text{La}_2\text{Mo}_2\text{O}_9$ type structure can be used to depict other structural effects. It also gives a deeper insight in the adequacy of this structural type for anion conduction.

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Keywords: tungsten substituted lanthanum molybdate, neutron powder diffraction, fast-ion conductors

MS53.27.5*Acta Cryst.* (2005). A61, C70**Interstitial Oxygen in Oxy-apatites**Miguel A.G. Aranda, Laura Leon-Reina, Enrique R. Losilla, *Departamento de Química Inorgánica, Universidad de Málaga,*

Oxide ion conductors are an important group of materials utilized as electrolytes in solid oxide fuel cell's (SOFCs), oxygen sensors, etc. Several families of oxide materials are being actively investigated including: i) fluorite-type (f.i. $\text{Y}_{0.16}\text{Zr}_{0.84}\text{O}_{1.92}$ and $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$); ii) perovskite-type (f.i. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$); and iii) oxy-apatite-type (f.i. $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$).

Lanthanide oxy-apatites display very high pure oxide ion conductivity likely due to an interstitial oxygen conduction mechanism instead of the common oxygen vacancy mechanism that operates in fluorite and perovskite oxide ion conductors.

We have used neutron powder diffraction (both constant-wavelength and time-of-flight data) [1,2] to determine the crystal structures of several lanthanum oxy-apatites at room and high temperatures. Some compositions have been analyzed by the Rietveld method including oxygen-stoichiometric materials ($\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$, $\text{La}_{9.33}(\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_4)_6\text{O}_2$, $\text{La}_{9.50}(\text{Ge}_{0.916}\text{Al}_{0.083}\text{O}_4)_6\text{O}_2$, $\text{La}_8\text{Sr}_2(\text{SiO}_4)_6\text{O}_2$ and $\text{La}_8\text{Sr}_2(\text{GeO}_4)_6\text{O}_2$) and oxygen-excess materials ($\text{La}_{9.55}(\text{SiO}_4)_6\text{O}_{2.32}$ and $\text{La}_{9.60}(\text{GeO}_4)_6\text{O}_{2.40}$). The presence of the interstitial oxygen for some compositions will be highlighted including its structural consequences. Finally, the relationship between the interstitial oxygen and the high-oxide ion conductivity properties will be emphasized.

[1] Leon-Reina L., et al., *J. Mater. Chem.*, 2004, **14**, 1142. [2] Leon-Reina L., et al., *J. Mater. Chem.*, 2005, **15**, submitted.

Keywords: fuel cells, oxide electrolytes, neutron diffraction

MS54 CRYSTALLOGRAPHY AT CONDITIONS OF EARTH AND PLANETARY INTERIORS*Chairpersons:* Guillaume Fiquet, Artem Oganov**MS54.27.1***Acta Cryst.* (2005). A61, C70**Phase Transformation in FeO under Deep Mantle Conditions**Takehiko Yagi, Nobuyoshi Miyajima, *Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan.* E-mail: yagi@issp.u-tokyo.ac.jp

Numerous studies have been made on the phase transformation in FeO under deep mantle conditions. However, the results are still controversial. We have studied the transition using both powdered FeO and single crystal of olivine-structured Fe_2SiO_4 (fayalite) as starting materials. High pressure and high temperature in situ X-ray diffraction studies were carried out at the Photo Factory, Tsukuba, to clarify the stability of B1-B8-rhombohedral phase boundaries. Basic results are consistent with that reported by Kondo et al. [1].

In order to get homogeneous Debye rings of the high-pressure phase of FeO, single crystal of fayalite was used as starting material. Sudden change in color accompanied with the change in X-ray diffraction pattern was observed during room temperature compression at around 30 GPa. Clear diffraction spots from crystalline phase were observed even at 80 GPa. This result is in contrast with the previous report that powdered fayalite becomes amorphous at around 40 GPa when compressed at room temperature [2, 3].

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Keywords: FeO, phase transition, high pressure

MS54.27.2*Acta Cryst.* (2005). A61, C70-C71**Compressibility and Structural Evolution of Post-perovskite Phase under Pressure**Thomas S. Duffy^a, Atsushi Kubo^a, Sean R. Shieh^b, Guoyin Shen^c, Vitali B. Prakapenka^c, ^a*Princeton University, New Jersey, USA.* ^b*National Cheng Kung University, Taiwan.* ^c*GSECARS, University of Chicago, Illinois, USA.* E-mail: duffy@princeton.edu

The post-perovskite (ppv) phase of $(\text{Mg,Fe})\text{SiO}_3$ is of major significance for understanding the D" layer at the base of Earth's