

**MS53.27.3***Acta Cryst.* (2005). A61, C70**Hydrogen Storage in light complex Hydrides – structural studies**Bjørn C. Hauback<sup>a</sup>, Hendrik W. Brinks,<sup>a</sup> <sup>a</sup>*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  $\text{AlH}_4^-$  unit, are among the most promising metal hydrides for reversible hydrogen storage. The storage capacity is large, e.g.  $\text{NaAlH}_4$  can release 5.6 wt% hydrogen below 200 °C. Work during the last years has revealed that Ti additives improve the kinetics of  $\text{NaAlH}_4$  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  $\text{MAID}_4$ , (M=Li, Na, K)  $\text{Li}_3\text{AlD}_6$ ,  $\text{Mg}(\text{AlH}_4)_2$  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.  $\text{NaAlH}_4$  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.  $\text{LiAlD}_4$  has been shown to decompose completely to LiD, Al and  $\text{D}_2$  at 127 °C, releasing 7.9 wt% hydrogen. Addition of  $\text{VCl}_3$  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<sup>a</sup>, Gwenaél Corbel<sup>a</sup>, Yvon Lalignat<sup>a</sup>, François Goutenoire<sup>a</sup>, Emmanuelle Suard<sup>b</sup>, <sup>a</sup>*Laboratoire des Oxydes et Fluorures, UMR CNRS 6010, Université du Maine, 72085 Le Mans cedex 9, France.* <sup>b</sup>*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  $\beta$ -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  $\beta$ - $\text{La}_2\text{Mo}_2\text{O}_9$  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.

[1] Lacorre P., et al, *Nature*, 2000, **404**, 856. [2] Corbel G., et al., *Chem. Mater.*, submitted. [3] Georges S., et al., *J. Mater. Chem.*, 2003, **13**, 2317.

**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  $\text{Fe}_2\text{SiO}_4$  (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].

[1] Kondo et al., *Phys. Earth Planet. Inter.*, 2004, **143-144**, 201-213. [2] Richard, Richet, *Geophys. Res. Lett.*, 1990, **17**, 2093-2096. [3] Andrault et al., *Phys. Chem. Minerals*, 1995, **22**, 99-107.

**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<sup>a</sup>, Atsushi Kubo<sup>a</sup>, Sean R. Shieh<sup>b</sup>, Guoyin Shen<sup>c</sup>, Vitali B. Prakapenka<sup>c</sup>, <sup>a</sup>*Princeton University, New Jersey, USA.* <sup>b</sup>*National Cheng Kung University, Taiwan.* <sup>c</sup>*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