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Hydrogen Storage in light complex Hydrides – structural studies
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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 $MAlD_4$, (M=Li, Na, K) Li_3AlD_6, $Mg(AlH_4)_2$ and mixed alanates, like Na_2LiAlD_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 indication the presence of an $Al_{1-x}Ti_x$ 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

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Structural Analysis of $La_2Mo_2O_9$-based fast Oxide-ion Conductors
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Most substitutes to La or Mo in fast oxide-ion conductor $La_2Mo_2O_9$ [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 $La_2Mo_{2-x}Cr_xO_9$ series [2].

The only known exception to this general trend is the series $La_2Mo_{2-x}W_xO_9$, 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 $La_2Mo_2O_9$ [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-$La_2Mo_2O_9$ 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

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Interstitial Oxygen in Oxy-apatites
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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. $Y_{0.16}Zr_{0.84}O_{1.92}$ and $Gd_{0.2}Ce_{0.8}O_{1.9}$); ii) perovskite-type (f.i. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$); and iii) oxy-apatite-type (f.i. $La_{9.33}(SiO_4)_6O_2$).

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 ($La_{9.33}(SiO_4)_6O_2$, $La_{9.33}(Si_{0.5}Ge_{0.5}O_4)_6O_2$, $La_{9.50}(Ge_{0.916}Al_{0.083}O_4)_6O_2$, $La_8Sr_2(SiO_4)_6O_2$ and $La_8Sr_2(GeO_4)_6O_2$) and oxygen-excess materials ($La_{9.55}(SiO_4)_6O_{2.32}$ and $La_{9.60}(GeO_4)_6O_{2.40}$). 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.

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Keywords: fuel cells, oxide electrolytes, neutron diffraction

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MS54 CRYSTALLOGRAPHY AT CONDITIONS OF EARTH AND PLANETARY INTERIORS
Chairpersons: Guillaume Fiquet, Artem Oganov

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Phase Transformation in FeO under Deep Mantle Conditions
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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].

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

MS54.27.2
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Compressibility and Structural Evolution of Post-perovskite Phase under Pressure
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The post-perovskite (ppv) phase of $(Mg,Fe)SiO_3$ is of major significance for understanding the D" layer at the base of Earth's

mantle. Here we report equation of state (EoS) and Rietveld refinement data of MgGeO3-ppv phase (CaIrO3-type, Cmcm) together with EoS data of silicate-ppv phase experimentally determined for the first time.

Germanate and silicate ppv phases were synthesized from MgGeO3 and Mg0.9Fe0.1SiO3 orthopyroxene at 86 GPa, ~1600 K and 103 GPa, ~1900 K, respectively, using laser-heated diamond cells with Ar or NaCl pressure medium. Angle-dispersive X-ray diffraction experiments were conducted at 13-ID-D, Advanced Photon Source. EoS data (bulk modulus, its pressure derivative, and room pressure unit cell volume) were obtained using Birch-Murnaghan EoS to be 203(6) GPa, 4.4, 179.7(9) A^3 for MgGeO3-ppv and 219(5) GPa, 4.4, 164.9(6) A^3 for silicate-ppv. Rietveld refinement of MgGeO3-ppv was performed using GSAS/EXPGUI. A change in compression mechanism was found at ~45 GPa. Although b-axis is the most compressible axis in the pressure range investigated, it is significantly more compressible at the lower pressure range. The reason is explained by decrease of distortion of GeO6 octahedron in the lower pressure range, and by both increase of distortion of GeO6 octahedron and shortening of Mg-O distances in the higher pressure range.

Keywords: high-pressure phases, X-ray powder diffraction, Rietveld refinement

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Refinement of High Pressure Metrology to 150 GPa
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In static high pressure experiments, the pressure cannot be directly measured. Therefore, secondary pressure scales must be used, such as luminescence gauges (like ruby) and x-ray gauges (gold, platinum, MgO, etc.). The calibration of these gauges is a critical issue: for instance, geophysical studies of the Earth's mantle transition zone minerals under high pressure and temperature have revealed to be inconsistent because of the use of incompatible pressure gauges [1]. We have measured ambient temperature equations of state of 13 metals (Be, Al, Fe, Co, Ni, Cu, Zn, Mo, Ag, Ta, W, Pt, Au) under quasi-hydrostatic conditions in a diamond anvil cell, up to at least 65 GPa and at a maximum pressure of 153 GPa. The use of state of the art pressurizing and x-ray diffraction techniques [2] allowed us to obtain standard synchrotron x-ray diffraction accuracy in the volume determination to the maximum pressure. This data set can been used to re-calibrate the static pressure scale based on the ruby luminescence wavelength measurement [3]. The accuracy of various forms of luminescence wavelength vs. pressure in different pressure ranges will be discussed. In particular, this recalibration confirms recent suggestions of an underestimation of pressure by [3] at ultra-high pressure.

[1] Bina C.R., *Nature*, 2001, **411**, 536. [2] Dewaele A., et al., *Phys. Rev. B*, 2004, **70**, 94112. [3] Mao H.K., et al., *J. Geophys. Res.*, 1986, **91**, 4673.
Keywords: diamond anvil cells, high-pressure physics, X-ray diffraction

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Shock-Induced Superheating-Melting and Geophysical Implications
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Superheating is a metastable state with the long-range order of a solid sustained above the equilibrium melting temperature, and a rare phenomenon. The limit of superheating was attempted realistically by assuming an arbitrary critical nucleation rate [1]. Based on classical nucleation theory and supercooling experiments, we developed the systematics relating materials properties to the maximum superheating (supercooling) and heating (cooling) rates, consistent with shock wave experiments, molecular dynamics simulations and Landau-type models [2-5]. Superheating is more achievable under ultrafast heating rate. There are strong indications of superheating in shock experiments on translucent solids using optical pyrometry [6-8] and on single crystal Al during dynamic spallation [9].

High strain- and heating-rates experiments such as shock wave loading are an essential complement to diamond-anvil cell techniques for investigating translucent minerals and opaque metals [10]. We present an exhaustive survey on superheating-melting behavior of alkali halides, silicates and metals, and their geophysical implications.

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Keywords: superheating-melting, shock, molecular dynamics

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Predicting Crystal Structures of New High-pressure Mineral Phases
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We approached the problem of predicting crystal structures using three different methods: CMAES [1], Metadynamics [2,3] and Evolutionary Algorithms [4].

The different methods and their results for the high-pressure structures of MgSiO3 and MgCO3 will be presented and discussed. On the methodological side, we will focus on our implementation of an Evolutionary Algorithm based on spatial heredity and combined with local optimization. This algorithm proved to be an efficient way to tackle high dimensional problems such as crystal structure prediction and hence has a promising future in predicting, on a fully theoretical basis, new crystal structures under pressure.

[1] Hansen N., Ostermeier A., *Evol. Comp.* , 2001, **9**, 159. [2] Martonak R., Laio A., Parrinello M., *Phys. Rev. Lett.* , 2003, **90**, 075503. [3] Oganov A.R., Martonak R., Laio A., Raiteri P., Parrinello M., 2005, *in preparation*. [4] Michalewicz Z., Fogel D.B., *How to Solve It: Modern Heuristics.*, Springer, Berlin, 2004.
Keywords: structure prediction, global optimization, evolutionary algorithm

MS55 TIME RESOLVED DIFFRACTION
Chairpersons: Jianming Cao, Hervé Cailleau

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Laser-Plasma X-ray Sources and Their Applications
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A single atomic vibrational motion is on the order of 100 fs (1 fs=10^{-15} s), which sets the fundamental timescale of material in response to an external excitation. Using pump-probe approach and initiating the dynamics with an ultra-short laser pulse, the new tool of femtosecond X-ray diffraction provides a direct means of monitoring the atomic positions during photo-induced transition in materials on this fundamental timescale and with sufficient spatial resolution.

In this talk we will show on one side the first type of femtosecond X-ray source, based on the laser-plasma interaction on solid target [1], together with its applications in the study of non-thermal melting in semiconductor [2] and the direct measurement of coherent optical phonons [3].