MPa) of thermal expansion and phase behavior for some of these materials have made use of a new "Background reducing Internal Mask" to obtain Rietveld quality X-ray data from samples contained in substantial heated titanium pressure vessels. Our studies of local structure evolution in the negative thermal expansion material cubic $ZrMo_2O_8$ as it is heated at ambient pressure and amorphized on compression in a diamond anvil cell will also be discussed.

Keywords: high-pressure diffraction, thermal expansion, local structure

MS.05.3

Behavior of SiO2 in helium pressure medium

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Although helium has been widely used as a good hydrostatic pressure transmitting medium, it sometimes affects considerably to the compression behavior of minerals. Here we report an example that SiO2 glass becomes quite "rigid" when compressed in helium. We have compressed SiO2 glass in helium up to 10 GPa with a diamond-anvil cell [1]. Volume measurements of the bulk size show that SiO2 glass is much less compressible than normal when compressed in a helium medium, and the volume in helium at 10 GPa is close to the normal volume at 2 GPa. X-ray diffraction and Raman scattering measurements suggest that interstitial voids in SiO2 glass are prevented from contracting when compressed in helium. This is probably because a large amount of helium penetrates into these voids. The estimated helium solubility in SiO2 glass is very high and is between 1.0 and 2.3 mol per mole of SiO2 glass at 10 GPa, which shows marked contrast with previous models.

These results may affect discussions on the Earth's evolution as well as interpretations of various high-pressure experiments, and also lead to the creation of new materials.

[1] T. Sato, N. Funamori, T. Yagi. **2011**, to be submitted.

Keywords: SiO2 glass, helium, voids

MS.05.4

### High-pressure polymorphism of ammonia hydrates

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Ammonia hydrates, $NH_3 \cdot nH_2O$ (where $n = \frac{1}{2}, 1, 2$), are likely to be major constituents of icy bodies in the outer solar system; their phase behaviour and physical properties up to pressures of several GPa are therefore relevant to modelling the structure and thermal evolution of such planetary objects [1]. We report the status of our program to investigate these properties using a combination of high-pressure powder diffraction (carried out at the ISIS neutron spallation source and the Institut Laue Langevin) and quantum mechanical calculations.

Calculations have provided us with predicted crystal structures, constrained only by the experimentally obtained unit-cell dimensions and contents, of both ammonia monohydrate phase II [2] and ammonia dihydrate phase II, as well as predicted structures of other high-pressure phases which can be tested against new powder diffraction data. Moreover, the elastic properties calculated by these methods are a direct complement to equations of state determined from high-pressure experiments [3], [4].

Most recently, we carried out an initial survey of the ammonia monohydrate phase diagram using a Paris-Edinburgh press on the high-intensity D20 beamline at the ILL. Neutron powder data collected over the five day study allowed us to fit an isothermal equation of state for ammonia monohydrate II over a range twenty times larger than previously measured, reproduced earlier observations [5] of phases IV and V, and constrained their phase transition pressures and temperatures (see figure below); ammonia monohydrate phase V was observed up to a pressure of 9 GPa. We will discuss the practical aspects of loading a volatile liquid sample into the CCR-mounted P-E press in use at the ILL, the nature and high quality of the data produced, and implications for our future studies of such systems at high pressure.

Figure 1 below shows the phase diagram of ammonia monohydrate, and the P-T path (pale line) followed during our December 2010 study at the ILL. The darker line shows the P-T path we propose to follow in future work.
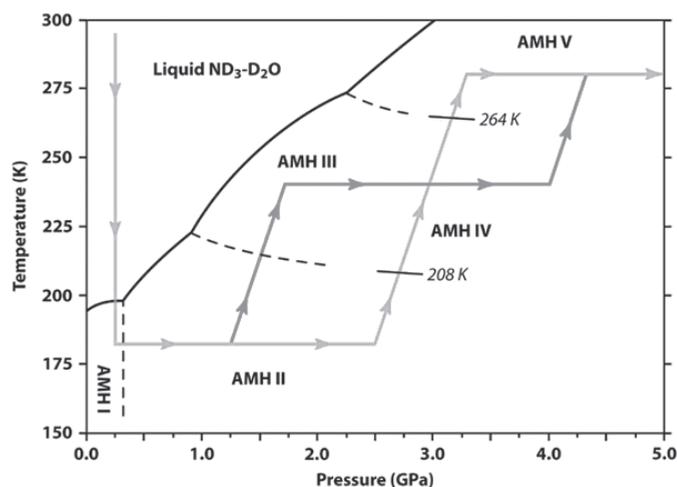
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Keywords: polymorphism, diffraction, pressure

MS.05.5

Structural Evolution of $Ca_{0.4}Sr_{0.4}Nd_{0.2}Mn_{1-x}Cr_xO_3$; $0 \leq x \leq 0.2$ perovskites

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A series of complex oxides of the type $Ca_{0.4}Sr_{0.4}Nd_{0.2}Mn_{1-x}Cr_xO_3$; x

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= 0 to 0.2 has been prepared and the evolution of the crystal structures studied using high-resolution powder X-ray and neutron diffraction. The amount of the Jahn-Teller active Mn^{3+} ions is controlled by partially replacing the Mn with Cr. At room temperature samples with x ≤ 0.05 only display out of phase rotations of the octahedral along c-axis leading to tetragonal $I4/mcm$ space group symmetry. Progressively replacing the Mn^{3+} with Cr^{3+} triggers additional rotations of the corner sharing octahedra ($a^-b^+a^-$ tilt system) such that samples with $x \geq 0.10$, adopt orthorhombic $GdFeO_3$-type structure in space group $Pbnm$. The lowering of symmetry upon addition of Cr is in response to the decrease in the effective size of the B-type cation (B = Mn and Cr). Equally importantly the Cr^{3+} acts to remove the Jahn-Teller type distortions induced by the presence of Mn^{3+}. High temperature diffraction measurements show that the increasing the magnitude of the tilts through the addition of Cr in $Ca_{0.4}Sr_{0.4}Nd_{0.2}Mn_{1-x}Cr_xO_3$ stabilizes an orthorhombic structure and a more complex sequence of phase transition is observed, namely $Pbnm \leftrightarrow I4/mcm \leftrightarrow Pm\underline{3}m$.

Keywords: phase_transition, perovskites, high_resolution_powder_diffraction

MS.06.1

Evolutionary crystal structure prediction: method and results

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While most of the known materials have been discovered through experiments, one wonders if theory will ever become capable of leading materials discovery. The evolutionary methodology USPEX [1] has been a major step towards this goal as it provides, given just the chemical composition and pressure/temperature conditions, the stable structure and a set of low-energy metastable structures. Important developments of this method were made thanks to the theory of energy landscapes [2].

Some of the applications are:

1. New stable high-pressure phase of boron, γ-B [3]. This superhard phase shows a surprising degree of charge transfer between boron sites, which affects many physical properties [3].

2. Transparent insulating phase of sodium [4] and new phases of calcium [5], $CaLi_2$ [6], nitrogen [7].

3. Unusual high-pressure behavior of methane CH_4, silane SiH_4 [8], germane GeH_4 [9] and stannane SnH_4 [10].

Many methodological developments happened recently. The method has been extended to molecular crystals, nanoparticles, and crystalline surfaces. It can now deal with systems with up to several hundred atoms in the unit cell. Its extension to variable-composition systems allows simultaneous finding of stable chemical compositions and the corresponding crystal structures in a multinary A-B-C… system. It is now also possible to optimize the structure and chemical composition with respect to a given physical property [11]. I will discuss newly predicted carbon allotropes with special properties.

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Keywords: USPEX, density functional theory, energy landscapes

MS.06.2

In silico crystallisations of organic molecules: what have we learnt?

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Since 1999, the blind tests for crystal structure prediction (CSP) have motivated the regular development and testing of CSP methodologies for small organic molecules. Blind tests' participants are sent the chemical diagrams of the target molecules and the experimental crystal structures are withheld until participants have submitted their predictions (three submissions per target). These communal experiments, organised regularly at the Cambridge Crystallographic Data Centre (CCDC), have recorded and tracked numerous challenges and successes over the years (1999 [1], 2001 [2], 2004 [3], 2007 [4] and 2010).

This talk will present the results of the 2010 blind test for CSP in which 15 research groups participated. Six different targets were attempted for prediction, three of which had a similar complexity to targets in previous blind tests: two small rigid molecules and one small flexible molecule. In addition to these, the 2010 blind test participants were challenged with the prediction of a 1:1 molecular salt, a highly flexible molecule and a polymorphic hydrate. The knowledge acquired over previous blind tests as well as the challenges faced in the present one will be discussed. Although there was no single method successful in all categories, every target had at least one successful prediction.

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Keywords: prediction, crystal, computation