

**MS22 P01****Exploring Polymorphism and Solvate Formation using**

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**Keywords:** Polymorphism, Intermolecular interaction, High pressure crystallisation

The application of high pressure to simple molecular compounds is proving to be a powerful method for exploring the polymorphic behaviour of these compounds [1, 2]. The principle behind this approach is that the structure of matter in the solid state is governed by intermolecular interactions and therefore the packing of molecules may be strongly affected by the application of pressure. High-pressure forms may be generated by direct compression of single crystals or powders, or by high-pressure crystallisation from the liquid state. However, these methods have some drawbacks when studying more complex organic compounds where kinetic barriers to interconversion may be high or where decomposition at high temperatures can occur. These problems may be overcome by pressure-induced crystallisation of organic compounds from solution to give either polycrystalline powders or single crystals, and this technique has yielded a number of new polymorphs and solvates that have not been previously observed at ambient pressure or *via* other high pressure techniques [3, 4]. This work has been extended and the poster will describe some of the results obtained from high-pressure crystallisation studies conducted on Stations 9.5HPT and 16.2 SMX in order to highlight how these high-pressure techniques can be used to explore polymorphism and solvate formation in a range of compounds.

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**MS22 P02****High-Pressure Structural, Electronic and Spin**

**Transitions in New Multiferroic GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>** I.S.

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**Keywords:** high pressure transformations, multiferroics, synchrotron radiation methods

High-pressure transformations in the single crystal and powdered samples of new multiferroic - gadolinium iron borate GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> have been studied in diamond anvil cells with the He pressure medium. GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> belongs

to the family of rare-earth borates RM<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (R is a rare-earth element, M = Al, Ga, Fe, Sc) and has the trigonal symmetry with the space group R32. The nonlinear optical and laser properties of these materials recently attracted a great attention to potential applications. GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> is an antiferromagnet with the Néel temperature  $T_N = 38$  K. The FeO<sub>6</sub> octahedra form helical one dimensional weakly coupled chains elongated along the c-axis. The Fe spin-flop transition occurs in the crystal at a temperature about 10 K, and the magneto-electrical effect appears at that transition due to changing magnetic symmetry. Thus, GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> can be considered as a new multiferroic material. In the present studies, along with high-pressure <sup>57</sup>Fe-Mössbauer transmission and Mössbauer synchrotron (NFS) spectroscopy, the X-ray diffraction and synchrotron high-resolution X-ray K<sub>β</sub> emission spectroscopy (XES), optical absorption and Raman scattering spectroscopy have been applied to study magnetic and structural properties, electronic and spin transitions at room and low temperatures. X-ray data show the first order structural transition at 25.6 GPa with collapse of the unit cell volume by 8%. Trigonal symmetry of the GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystal is retained at this transition. The second structural anomaly was observed near 43 GPa. Two electronic transitions have been found at the critical pressures ~26 GPa and ~43 GPa form optical absorption spectra. At first transition the optical gap drops from 3.10 to 2.25 eV, and at 43 GPa, the gap decreases to ~0.7 eV indicating the transition from the insulating to a semiconducting state. The low-temperature NFS spectra indicate that the Néel temperature of GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, which is 38 K at ambient pressure, is not essentially changed with pressure increase. From room-temperature NFS and XES experiments, the spin crossover in 3d electron system with the transition of Fe<sup>3+</sup> ions from the high-spin (HS)  $S = 5/2$  state to a low-spin (LS)  $S = 1/2$  state was found in the pressure range of 45-53 GPa. It is curious that the HS → LS transition occurs in the paramagnetic state of GdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> where a magnetic-order parameter differentiating the HS and LS states is absent. It was concluded that the observed broadening of the spin-crossover transition on pressure scale ( $\Delta P \sim 8$  GPa) is not an effect of nonhydrostaticity since we used He as the pressure medium. It is explained by thermal fluctuations between HS and LS states in the critical region of transition.

*This work is supported by Russian Foundation for Basic Research grant № 05-02-16142-a, by the Program of Russian Academy of Sciences "Strongly correlated electronic systems", and by the DOE grant DE-FG02-02ER45955, USA.*

**MS22 P03****The behavior of  $\alpha$ -K<sub>4</sub>CoMo<sub>3</sub>O<sub>12</sub> under high pressure** J.

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**Keywords:** high-pressure, structure systematics, molybdates

High-pressure X-ray single-crystal diffraction experiments on three different crystals of  $\alpha$ -K<sub>4</sub>Co(MoO<sub>4</sub>)<sub>3</sub> [1] were

performed in the pressure range between 0.2 and 7.9 GPa. For this purpose a diamond-anvil cell with methanol-ethanol mixture (in ratio 4:1) as pressure medium and tungsten gaskets were used [2].

In this pressure range we were able to solve the structures of three different high-pressure phases. The structures of these phases show a stepwise increase of MoO<sub>n</sub>-coordination from MoO<sub>4</sub>-tetrahedra via MoO<sub>5</sub>-pyramids to MoO<sub>6</sub>-octahedra with increasing pressure.

At approximately 1.3(2) GPa the first high-pressure phase K<sub>4</sub>Co(MoO<sub>4</sub>)<sub>3</sub>-II appeared with additional reflections in the a\*-c\*-plane of the initial unit cell, corresponding to a doubling of cell volume. Equivalent positions in the  $\alpha$ -phase split into inequivalent sites, but only minor changes in the structure are accompanied with this phase transition. At about 2.2(1) GPa the second high-pressure phase K<sub>4</sub>CoMo<sub>3</sub>O<sub>12</sub>-III was found, showing a change in the coordination of some molybdenum ions: Two neighbouring [MoO<sub>4</sub>]-tetrahedra transform to a pair of edge-sharing [MoO<sub>5</sub>]-pyramids. At about 5.97(5) GPa the third high-pressure phase K<sub>4</sub>CoMo<sub>3</sub>O<sub>12</sub>-IV appeared. More [MoO<sub>4</sub>]-tetrahedra have transformed into edge-sharing pairs of [MoO<sub>5</sub>]-pyramids and the [MoO<sub>5</sub>]-pyramids in phase -III have been transformed further into [MoO<sub>6</sub>]-octahedra. The [CoO<sub>6</sub>]-octahedra remain in all phases and are only slightly affected by the application of hydrostatic pressure.

This work is part of a systematic study of complex network structures in quaternary phases A-T-Mo-O with A an alkaline metal and T a 3d-transitional metal.

Financial support from DFG (EH 183/2) is gratefully acknowledged.

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#### MS22 P04

**Structures of high-pressure polymorphs: what can different techniques contribute to our knowledge about them? (Crystals of selected amino acids as examples).** E.V. Boldyreva<sup>a,b</sup>, H. Sowa<sup>c</sup>, H. Ahsbahs<sup>d</sup>, V.V. Chernyshev<sup>e</sup>, Yu.V. Seryotkin<sup>a,f</sup>, N.A. Tumanov<sup>a,b</sup>, V.P. Dmitriev<sup>g</sup>, S.V. Goryainov<sup>a,f</sup>, H.Bordallo<sup>h</sup>, <sup>a</sup>REC-008 Novosibirsk State University, Russia, <sup>b</sup>Institute of Solid State Chemistry and Mechanochemistry SB RAS, <sup>c</sup>University of Goettingen, Germany, <sup>d</sup>University of Marburg, Germany, <sup>e</sup>Moscow State University, Russia, <sup>f</sup>Institute of Geology and Mineralogy SB RAS,

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**Keywords: polymorphism, high pressure, amino acids**

Effect of pressure on the crystalline amino-acids has recently become a hot topic: i) monitoring pressure-induced structural distortions / phase transitions gives a better insight into the intermolecular interactions / intramolecular dynamics in these systems, which can mimic the conformational changes of biopolymers, ii) the control of the polymorphism is important for many applications, for example, for the pharmaceutical industry. Typically, Raman spectroscopy, X-ray, or, more rarely, neutron powder diffraction are used, to characterize the

structures of the new high-pressure forms. In some lucky cases, it is possible to get a single crystal intact through the phase transition, and then a single-crystal diffraction technique can be used. Each of the techniques has its advantages and limitations.

The aim of the present contribution is to compare the results obtained during a few recent years for the same systems studied independently by several research groups in Russia, Germany, UK, India using different experimental techniques. In particular, we compare the complementary knowledge on the high-pressure polymorphs of glycine gained by X-ray powder diffraction, X-ray single-crystal diffraction, Raman spectroscopy and inelastic neutron scattering, as well as the results of the studies of L- and DL-serine by X-ray powder diffraction, neutron powder diffraction, X-ray single crystal diffraction, Raman spectroscopy and inelastic neutron scattering.

This work was supported by a 05-03-32468 grant from RFBR, a grant from BRHE (RUX0-008-NO-06), and #49 and #110 Integration Projects of SB RAS.

#### MS22 P05

**Pressure-induced structural phase transition and negative thermal expansion in ReO<sub>3</sub>** Tapan Chatterji<sup>a</sup>, G.J. McIntyre<sup>a</sup>, H.E. Fischer<sup>a</sup>, M. Brunelli<sup>b</sup>, <sup>a</sup>Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex, France, <sup>b</sup>European Synchrotron Radiation Facility, BP 222, 38043 Grenoble Cedex, France. E-mail: [chatterji@ill.fr](mailto:chatterji@ill.fr)

**Keywords: High pressure, negative thermal expansion, structural phase transition.**

We have investigated the pressure-induced structural phase transition in ReO<sub>3</sub> by neutron diffraction on a single crystal. We collected neutron diffraction intensities from the ambient and high pressure phases at T = 7 kbar and refined the crystal structures. We have determined the stability of the high pressure phase as a function of temperature down to T = 2 K and have constructed the (P-T) phase diagram. The critical pressure is P<sub>c</sub> = 5.2 kbar at T = 300 K and decreases almost linearly with decreasing temperature to become P<sub>c</sub> = 2.5 kbar at T = 50 K. The phase transition is driven by the softening of the M<sub>3</sub> phonon mode. The high pressure phase is formed by the rigid rotation of almost undistorted ReO<sub>6</sub> octahedra and the Re-O-Re bond angle deviates from 180 degree. We do not see any evidence for the existence of the tetragonal (P4/mbm) intermediate phase reported earlier. In order to

check whether Re-O-Re bond angle deviate from 180 degree in the local structure we have determined neutron diffraction intensities up to a very high Q as a function of pressure from a polycrystalline sample of ReO<sub>3</sub> on a hot neutron diffractometer. The preliminary PDF analysis indicates that the Re-O-Re bond angle deviate from 180 degree already at ambient pressure. We have also determined the thermal expansion of ReO<sub>3</sub> on a high resolution X-ray powder diffractometer at the synchrotron source in the temperature range 4-500 K and discovered negative thermal expansion in the low temperature range 4-120 K. The negative thermal expansion in ReO<sub>3</sub> is attributed to the rigid unit M<sub>3</sub> phonon mode.