

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

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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.

[1] F.P.A. Fabbiani and C.R. Pulham, *Chem. Soc. Rev.* (2006), 35, 932-942.

[2] S.A. Moggach, D.R. Allan, S.J. Clark, M.J. Gutmann, S. Parsons, C.R. Pulham, and L. Sawyer, *Acta Cryst.*, (2006), B62, 296-309.

[3] F.P.A. Fabbiani, D.R. Allan, A. Dawson, W.I.F. David, P.A. McGregor I.D.H. Oswald, S. Parsons, and C.R. Pulham C. R., *Chem. Commun.*, (2003), 3004.

[4] F. P. A. Fabbiani, D. R. Allan, S. Parsons and C. R. Pulham, *CrystEngComm.* (2005), 7, 179.

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

Transitions in New Multiferroic GdFe₃(BO₃)₄ [I.S.](#)

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High-pressure transformations in the single crystal and powdered samples of new multiferroic - gadolinium iron borate GdFe₃(BO₃)₄ have been studied in diamond anvil cells with the He pressure medium. GdFe₃(BO₃)₄ belongs

to the family of rare-earth borates RM₃(BO₃)₄ (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. GdFe₃(BO₃)₄ is an antiferromagnet with the Néel temperature $T_N = 38$ K. The FeO₆ 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, GdFe₃(BO₃)₄ can be considered as a new multiferroic material. In the present studies, along with high-pressure ⁵⁷Fe-Mössbauer transmission and Mössbauer synchrotron (NFS) spectroscopy, the X-ray diffraction and synchrotron high-resolution X-ray K_β 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 GdFe₃(BO₃)₄ 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 GdFe₃(BO₃)₄, 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 Fe³⁺ 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 GdFe₃(BO₃)₄ 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.

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MS22 P03**The behavior of α -K₄CoMo₃O₁₂ under high pressure** [J.](#)

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High-pressure X-ray single-crystal diffraction experiments on three different crystals of α -K₄Co(MoO₄)₃ [1] were