FA2-MS19-P01

High-pressure behavior of bismuth iron oxide $Bi_2Fe_4O_9$. <u>Jasmin Biehler</u>[a], Alexandra Friedrich[a], Wolfgang Morgenroth[a], Leonore Wiehl[a], Björn Winkler[a], Michael Hanfland[b], Martin Tolkiehn[c], Manfred Burianek[d], Manfred Mühlberg[d]. [a]*Inst. of Geosciences, Crystallography, Goethe-University Frankfurt am Main, Germany.* [b]*ESRF, Grenoble, France.* [c]*DESY/HASYLAB, Hamburg, Germany.* [d]*Inst. of Crystallography, University of Cologne, Germany.*
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$Bi_2Fe_4O_9$ belongs to the mullite-related compounds $Bi_2M_4O_9$ (with M = Fe, Al, Ga) [1]. It melts incongruently and single crystals were grown from high temperature solutions using the top seeded solution growth method (TSSG) [2]. $Bi_2Fe_4O_9$ has interesting magnetic properties and shows a magnetic transition at about 264 K from paramagnetism to antiferromagnetism [3]. We are interested in the behaviour of the stereochemically active Bi^{3+} lone electron pair, which exists in the crystal structure of the compounds, at ambient and high pressure and of the effect of cation substitution on the compressibility and the occurrence of a reversible phase transition. In this study, the high-pressure behaviour of $Bi_2Fe_4O_9$ was analysed by in-situ powder and single-crystal X-ray diffraction and Raman spectroscopy. Pressures up to 34.33(8) GPa were generated using the diamond anvil cell technique. The occurrence of a reversible phase transition, analogous to that observed in isotypic $Bi_2Ga_4O_9$ [4,5] from space group *Pbam* to *Pbnm* (with c' = 2c) was confirmed in $Bi_2Fe_4O_9$ at 6.89(6) GPa from powder diffraction experiments and validated with Raman measurements. The high-pressure structure is stable at least up to 26.3(1) GPa. A fit of a 2nd-order Birch-Murnaghan equation of state to the *p-V* data results in K_0 = 74(3) GPa for the low-pressure phase and 79(2) GPa for the high-pressure phase. The Grüneisen-parameters for several modes are obtained from the Raman-spectroscopic measurements. The crystal structures of the low- and high-pressure phases were refined from single-crystal data at ambient conditions and at 100 K and at pressures of 4.49(2), 6.46(2), 7.1(1), 7.26(2) and 9.4(1) GPa. The influence of cation substitution on the high-pressure stability of the $Bi_2M_4O_9$ compounds will be discussed.

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Keywords: high-pressure X-ray diffraction, Raman spectroscopy, diamond anvil cells

FA2-MS19-P02

Self-assembly of fundamental building blocks (FBB) in borate structures. Rimma Bubnova[a], Stanislav Filatov[b]. [a]*Institute of Silicate Chemistry of the RAS, St. Petersburg, Russia.*
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One of distinguishing characteristic of unique borate crystal chemistry is occurrence of rigid groups consisting of the BO_3 triangles and the BO_4 tetrahedra (nanogroups about 0.6–1 nm). These rigid groups that constitute the fundamental building blocks (FBBs) maintain their configuration in various crystal structures without any essential changes. Moreover it is shown [1, 2] that on heating the BO_3 and BO_4 polyhedra and the FBBs maintain the size and configuration also. The great diversity of borate crystal structures arises from FBBs condensed to form structures of 0D-, 1D-, 2D and 3D-dimensionality. Here we present self-assembly of FBBs in borate structures as a result of thermal vibrations of boron and oxygen atoms and FBBs.

In a BO_3 triangle oxygen and boron atoms oscillate mainly perpendicular to the B–O bond. There are three B–O bonds in the BO_3 triangle, thus B and O atoms vibrate maximally perpendicular to the BO_3 plane. In the case of a triborate group composed of three triangles B and O atoms vibrate maximally perpendicular to the plane of the triborate group. Hence a structure with isolated triborate groups expands greatly perpendicular to plane of a group and expands weakly in parallel to plane of a group: as example we examine the same character of thermal expansion of α- and β-BaB_2O_4 crystal structures built up from isolated triborate groups. Moreover the triborate groups are usually self-arranged by parallel to each other in the 0D-3B-structures. Similar situation occurs in structures with isolated tetra- and pentagroups although in last case the internal oxygen and boron atoms of both single rings vibrate perpendicular to planes of these rings group while a group as a whole oscillates relative axis of the group – the line drawn parallel to the plane of both rings. From this viewpoint we examine the role of thermal vibrations anisotropy in borate structure formation any dimensionality.

[1] Bubnova R.S., Filatov S.K. *Phys. Stat. Sol.* 2008, 245(b), 2469. [2] Bubnova R.S., Filatov S.K. High-Temperature Crystal Chemistry of Borates and Borosilicates. 2008, St. Petersburg, Nauka (in Russ.).

Keywords: high-temperature crystal chemistry, borates, thermal expansion, single-crystal and powder high-temperature diffraction

FA2-MS19-P03

Studies on the decomposition of tungsten hexacarbonyl, $W(CO)_6$. <u>Nadine Rademacher</u>[a], Lkhamsuren Bayarjargal[a], Björn Winkler[a], Hyunjeong Kim[b], Katharine Page[b], Thomas Proffen[b]. [a]*Inst. of Geosciences, University of Frankfurt, Germany.* [b]*Los Alamos National Laboratory, Lujan Neutron Scattering Center, USA.*
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Tungsten hexacarbonyl is an important precursor molecule for the synthesis of micro- or nanocrystalline tungsten and tungsten compounds. In electron- or ion-beam deposition techniques, $W(CO)_6$ is used as a precursor for mask repair or nanolithography.[1] In order to better understand $W(CO)_6$ and its behaviour at a variety of reaction conditions, our group performed decomposition experiments in a laser heated diamond anvil cell (DAC) with pressures up to 17 GPa. Additional experiments at lower pressures and temperatures were performed in an autoclave. The decomposition products of $W(CO)_6$ have been characterised using Raman

spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and pair distribution function analysis (PDF). The analyses show that, depending on the reaction conditions, different products are formed. Some of these are nanocrystalline.
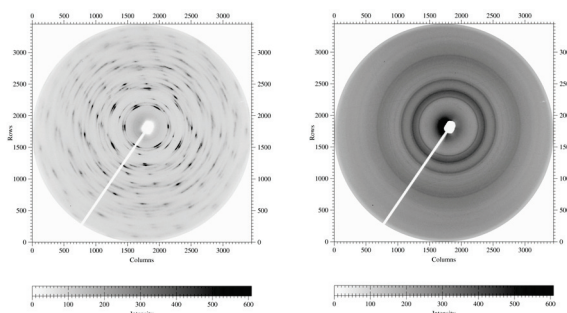

Fig. 1: Synchrotron X-ray diffraction patterns before (left) and after (right) laser heating W(CO)$_6$ in a diamond anvil cell.
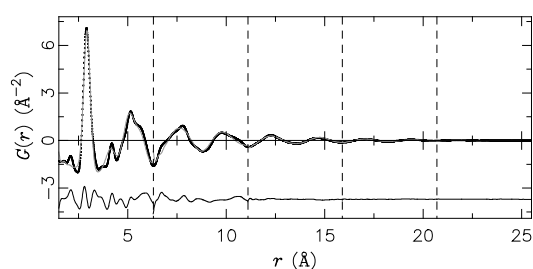

Fig. 2: PDF refinement results of the decomposition product obtained in the autoclave at lower pressures and temperatures. Note that the structural correlations end at about 2-2.5 nm.

[1] Porrati, F.; Sachser, R.; Huth, M.; *Nanotechnology*, 2009, 20, 195301.

Keywords: diamond anvil cells, decomposition, tungsten compounds

Full details of single crystal instrumentation and methodology are described in [3]. A sample was placed in a BGI design diamond anvil cell in ethanol:methanol (1:4) pressure transmitting media (steel gasket with a 350 microns hole preindented at 110 microns). For comparison, reference data were also collected for the same crystal at the same pressures using a Eulerian diffractometer equipped with a conventional X-ray source/optics [3]. The crystal size (180×120×50 mkm^3) was selected on the basis of its scattering power, such that the Bragg maxima were reasonably intense on the conventional system. In summary, we note that the lattice parameters measured using both diffractometers agree perfectly, lying within less than 2 estimated standard deviations.

Ultrasonic wave velocity measurements indicate that the dependency of the second order elastic stiffness tensor component C_{66} vs. P extrapolates to zero at 3.2 GPa [4]. The possibility of a phase transition was therefore suggested [4]. However, we observed no transition up to 7 GPa, which agrees with high pressure Raman scattering study [5]. F_E-f_E plot for Li$_2$B$_4$O$_7$ indicates a positive slop, therefore, a Birch-Murnaghan 3rd order EoS was fitted to the volume-pressure data (V_0=923.26(4) Å^3, K=46(1) GPa, K'=6.8(5)). Li$_2$B$_4$O$_7$ is more compressible along polar c-axis with β_0a:β_0c=1:3.04. Finally, relations between thermal expansion and compressibility of Li$_2$B$_4$O$_7$ will be presented.

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Keywords: high-pressure mineralogy-1, elastic properties-2, X-ray high-pressure techniques-3

FA2-MS19-P04

Compressional Behaviour of Diomignite, Li$_2$B$_4$O$_7$.
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Despite the fact that diomignite (Li$_2$B$_4$O$_7$, $I4_1cd$ symmetry) may control the physicochemical properties of highly fractionated late stage fluids in pegmatites [1], no diffraction studies concerning its compressional behaviour are available. In respect to technological importance, pegmatites are the primary source of lithium, which is widely employed in different fields of science and engineering (e.g. as a battery material, coolants for heat transfer applications etc.). Synthetic Li$_2$B$_4$O$_7$ can be implemented in acoustoelectronics, non-linear optics and piezotechnolodgy.

Compression of weakly scattering diomignite was also investigated for the purpose of commissioning an Eulerian single crystal diffractometer with an ultra high intensity rotating anode X-ray source equipped with multilayer optics [2]. This technique allows 8-position centring of Bragg reflections for accurate measurements of lattice parameters.

FA2-MS19-P05

Crystallographic Characterisation of Copper Based Shape Memory Alloys. Osman Adiguzel, *Firat University, Department of Physics, Elazig/Turkey.*
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Shape-memory alloys are functional materials due to their unusual ability to "remember" the desired particular shapes at different temperatures. This ability arises from the characteristic microstructures in parent and product phases. These alloys exhibit a peculiar property called shape memory effect and involve the repeated recovery of macroscopic shape of material at different temperatures. The origin of this phenomenon lies in the fact that the material changes its internal crystalline structure with changing temperature.

Shape memory effect comprises crystallographically reversible transition from the high-temperature parent phase with high symmetry to low-temperature product phase, martensitic phase with low symmetry and exhibits dynamic recovery of the shape. This effect leads to a displacive transition, martensitic transition, which precedes through a series of metastable states in copper based shape memory alloys with changing temperature.

Copper-based alloys exhibit this property in β-phase field which has a bcc structure at high temperature parent phase. The high temperature bcc-structure undergoes two types of