ESRF	**Experiment title:** Compression mechanism of $Bi_2Ga_4O_9$ – an ionic conductor with a stereochemically active lone electron pair	**Experiment number**: HS-3256
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Report:

$Bi_2M_4O_9$ (M = Ga^{3+}, Fe^{3+}, Al^{3+}) and related compounds (e.g., $Bi_2Mn_4O_{10}$) belong to the family of mullite-type crystal structures and exhibit interesting properties and structural features, such as high oxygen ion conductivity and a well-localised and stereochemically-active lone electron pair of the Bi^{3+} ion [1]. We are interested in the compressibility and high-pressure stability of these compounds. Our earlier calculations on the structural compression of $Bi_2Ga_4O_9$ up to 50 GPa using density functional theory (DFT) predicted a very unusual compression behaviour at pressures between 15 and 25 GPa. However, an attempt to infer the existence of a structural phase transition at this pressure would have been extremely time consuming. Hence, we planned to use high pressure diffraction experiments in order to investigate the predicted compression behaviour.

We performed *in situ* high-pressure powder diffraction experiments up to pressures of 35 GPa using synchrotron X-ray radiation at a wavelength of 0.3738 Å and a MAR345 image plate system. The samples were loaded into LeToullec diamond anvil cells using helium or neon as a pressure-transmitting medium. The images were processed and integrated with *FIT2D* [2]. *LeBail* refinements were carried out with *GSAS* [3].

We investigated the high-pressure behaviour of the isotypic compounds $Bi_2Ga_4O_9$ [*Pbam*, a = 7.9360(1) Å, b = 8.3021(1) Å, c = 5.8985(1) Å, V = 388.625(8) Å³] and $Bi_2Al_4O_9$ [V = 356.91(1) Å³], and of structurally-related $Bi_2Mn_4O_{10}$ [V = 372.27(1) Å³] up to 35, 30 and 35 GPa, respectively. A phase transition was detected in $Bi_2Ga_4O_9$ at around 16 GPa (Figure 1, left), which is accompanied by distinct changes in the pressure evolution of the

lattice parameters. The phase transition is reversible without a noticeable hysteresis. The space group symmetry is reduced to *Pbnm* (a = 7.2436(6) Å, b = 8.1378(4) Å, c = 11.5677(9) Å at 16.07(4) GPa) following a group-subgroup relationship accompanied with a doubling of the c axis, and hence of the unit-cell volume. A further analysis of the data using Landau theory is currently in progress. The transition pressure coincides well with the pressure range of structural changes predicted by DFT calculations. Also, the pressure evolution of the cell parameters agrees well between experiment and theory, with the b and c axes increasing and the a axis and unit-cell volume decreasing at the observed change in compression. In contrast to the DFT results, however, the structure of the low-pressure phase is not stable up to 50 GPa (as was predicted by DFT), but transforms to a high-pressure phase at 16 GPa.

Both further investigated compounds ($Bi_2Al_4O_9$ and $Bi_2Mn_4O_{10}$) are less compressible than $Bi_2Ga_4O_9$ and stable to the highest pressure obtained (Figure 1, right). They neither show an anomalous behaviour nor a phase transition. In $Bi_2Mn_4O_{10}$ this stability might be explained by the incorporation of an additional oxygen atom in the crystal structure. The stability of $Bi_2Al_4O_9$ to at least 30 GPa without indication of a phase transition is surprising, although a higher transition pressure would have been expected. In summary, the cation substitution has a huge effect on the high-pressure stability of these compounds.

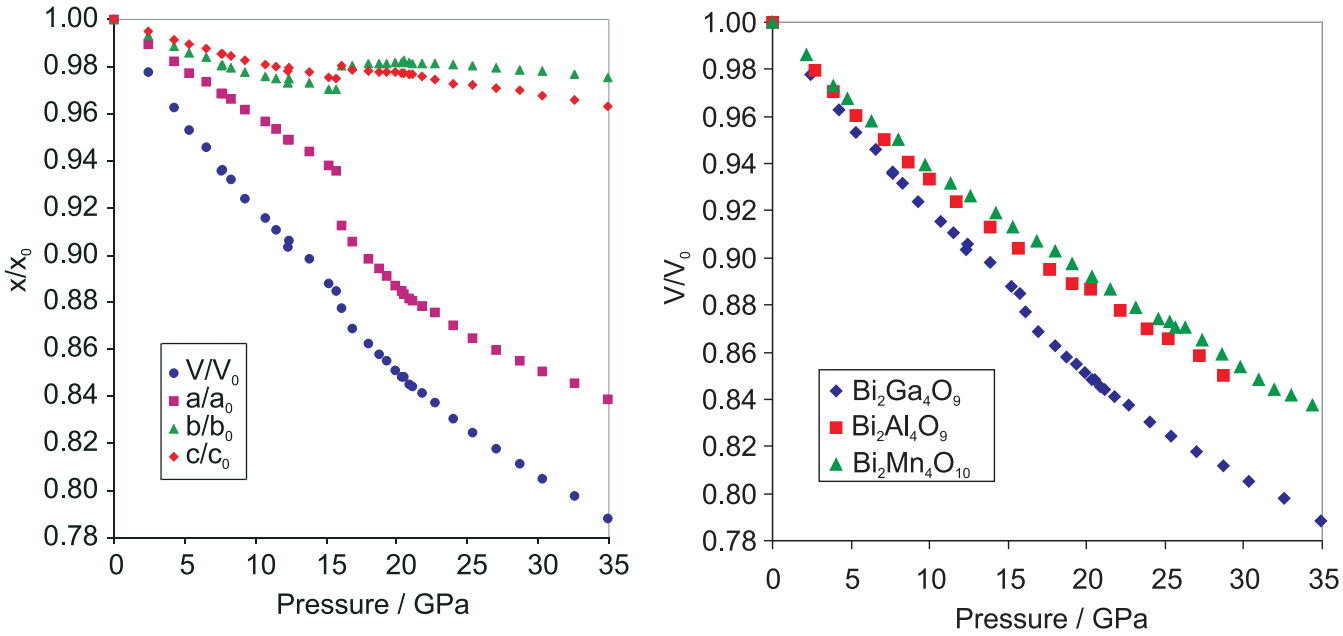

Figure 1. *Left:* Pressure dependencies of the normalized unit-cell parameters of $Bi_2Ga_4O_9$. Discontinuities indicate a reversible phase transition at 16 GPa. The c axis and volume, V, of the high-pressure phase are normalized by $c/2c_0$ and $V/2V_0$ for comparison. *Right:* Bulk compression of the three investigated compounds. $Bi_2Ga_4O_9$ is more compressible than $Bi_2Al_4O_9$ and $Bi_2Mn_4O_{10}$, which are structurally stable.

Literature:

[1] Abrahams, I, Bush, AJ, Hawkes, GE, and Nunes, T (1999) J. Solid State Chem. 147, 631.

[2] Hammersley, A (1998) FIT2D, Version 10.27, Reference Manual, ESRF, Grenoble, France.

[3] Larson, AC and Von Dreele, RB (1994) Los Alamos National Laboratory Report LAUR, 86–748.