ESRF	**Experiment title:** What is the stereochemical role of the Bi(III) lone electron pair at high pressure?	**Experiment number:** HS-3670
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Report:
In Bi^{3+} compounds the outer-shell *s*-electrons of the Bi^{3+} ion are often localised as non-bonding lone electron pairs on one side of the ion. This configuration is often stereochemically active and leads to unusual and interesting physical properties, e.g. the photorefractive properties of sillenites [1]. The stereochemical activity of lone electron pairs is interesting as more than half of all acentric oxides contain lone electron pairs [2]. It is generally assumed that high pressure can be used to induce changes of the electronic structure (like a symmetrisation of the electron distribution, or semiconducting or metallic behaviour) as non-binding electron pairs are known to be much more compressible than ions of equivalent size (e.g. oxygen ions), which in general leads to an anisotropic compression. With this project we aimed to elucidate the stereochemical role of the Bi^{3+} lone electron pair at high-pressure. In particular, the high-pressure stability and compressibility of the cubic silllenites $Bi_{12}MO_{20}$ (M = Si, Ge, Ti) and the orthorhombic mullite-related $Bi_2M_4O_9$ (M = Ga, Al, Fe) and $Bi_2Mn_4O_{10}$ (see ESRF report HS-3256, [3]) were studied. Sillenites are non-centrosymmetric oxides with space group I23. As an anisotropic compression cannot occur in the cubic sillenites it is very interesting to understand if this leads to a "geometrical frustration" similar to pyrochlores [4]. In a previous study at ESRF we have already shown that $Bi_2Al_4O_9$ and structurally related $Bi_2Mn_4O_{10}$ are stable up to 29 GPa and 35 GPa, respectively, while $Bi_2Ga_4O_9$ shows a phase transition at 16 GPa [5]. Further structure analyses and quantum mechanical calculations showed that the misfit of Ga in tetrahedral coordination is the driving force for the phase transition. Hence, we have predicted a phase transition in $Bi_2Fe_4O_9$ at a comparatively low pressure.

We performed *in situ* high-pressure powder diffraction experiments on $Bi_{12}SiO_{20}$ (BSO), $Bi_{12}GeO_{20}$ (BGO), $Bi_{12}TiO_{20}$ (BTO) and $Bi_2Fe_4O_9$ up to pressures of 50 GPa using synchrotron X-ray radiation at a wavelength of 0.4141 Å and a MAR555 flat panel detector. The samples were loaded into diamond anvil cells (DACs) using neon or helium as a pressure-transmitting medium in our institute (BSO, BTO and $Bi_2Fe_4O_9$) and at ESRF (BGO and $Bi_2Fe_4O_9$). Pressure was determined by means of the laser-induced ruby-fluorescence technique. The images were processed and integrated with FIT2D [6]. LeBail refinements were carried out with GSAS [7]. The bulk moduli B_0 and their pressure derivatives B' were determined by fitting 3^{rd}-order Birch-Murnaghan equations of state to the data.

The pressure dependence of the unit cell volumes of the sillenites BSO, BGO and BTO is shown in Figure 1. The equation-of-state fits resulted in $B_0 = 57(2)$ GPa and $B' = 9.0(4)$ for BSO, $B_0 = 63.0(5)$ GPa and $B' = 5.90(7)$ for BGO and $B_0 = 50(1)$ GPa and $B' = 8.6(3)$ for BTO. The three sillenites show a similar compressibility. Hence, the cation substitution seems to have no significant influence on the high-pressure properties. No indication for a phase transition was observed in the investigated pressure range up to 40 GPa, 50 GPa and 37 GPa for BSO, BGO and BTO, respectively. This shows the high stability of the cubic sillenite structure at high pressure and makes us assume that the stereochemical activity of the Bi^{3+} lone electron pairs persists at least up to 50 GPa.

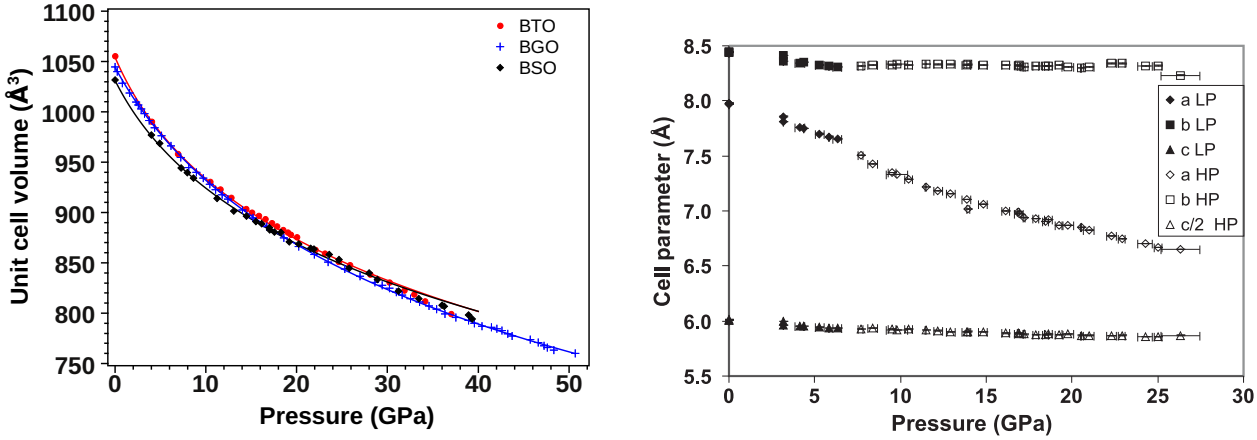

Fig. 1. Pressure dependence of the unit cell volume of BSO, BGO and BTO (left) and of the unit cell parameters of $Bi_2Fe_4O_9$ (right). The lines represent the Birch-Murnaghan equation of state fits of 3^{rd} order (left).

We have measured $Bi_2Fe_4O_9$ up to 26 GPa and detected an analogous phase transition to that of $Bi_2Ga_4O_9$ at lower pressure of about 7 GPa (Fig. 1, [8]). This agrees with the larger ionic radius of Fe^{3+} compared to that of Ga^{3+} and confirms the mechanism of phase transition. Hence, it is not due to a loss of the stereochemical activity of the lone electron pair, which persists up to pressures of at least 50 GPa [5]. The *c* axis is doubled at the phase transition and the symmetry is reduced in a group-subgroup relationship from space group *Pbam* to *Pbnm*. Clearly, in these compounds the cation substitution has a strong effect on the high-pressure stability.

Concluding, we have shown that the stereochemical activity of the lone electron pair of Bi^{3+} persists up to about 50 GPa in the sillenites and the mullite-related ternary bismuth oxides and that it is much more stable than was previously suggested. Further, the cation substitution does not strongly affect the high-pressure behaviour of the investigated sillenites, but has a strong influence on that of the mullite-related ternary bismuth oxides.

References

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