Pressure-induced phase transition in $Pb_6Bi_2S_9$

L. A. Olsen[a], K. Friese[b], E. Makovicky[a], T. Balić-Žunić[a], W. Morgenroth[c], A. Grzechnik[b]

a Department of Geography and Geology, University of Copenhagen, Copenhagen, Denmark
b Departamento de Física de la Materia Condensada, Universidad del País Vasco, Bilbao, Spain
c Institut für Geowissenschaften, FE Mineralogie, Abt. Kristallographie, Universität Frankfurt, Germany

Heyrovskyite (*Bbmm*, $Z = 4$) is the stable phase of $Pb_6Bi_2S_9$ at ambient conditions and is built from distorted moduli of PbS-archetype structure with a low stereochemical activity of the Pb^{2+} and Bi^{3+} lone electron pairs (Figure 1). The moduli are cut parallel to $(311)_{PbS}$ and combined by mirror planes parallel to (010) of heyrovskyite. The width of the moduli can be evaluated by counting the number of PbS octahedra running across each slab parallel to $[011]_{PbS}$. Heyrovskyite is a member of the lillianite homologous series which is based on various thicknesses of the above defined slabs. Each homologue type is symbolized as ${}^{N}L$ (N number of octahedra) or ${}^{N1,N2}L$ when there are two slabs of distinct thicknesses. Heyrovskyite is the ${}^{7}L$ member of the homologous series, whereas lillianite ($Pb_3Bi_2S_6$) is the ${}^{4}L$ member.

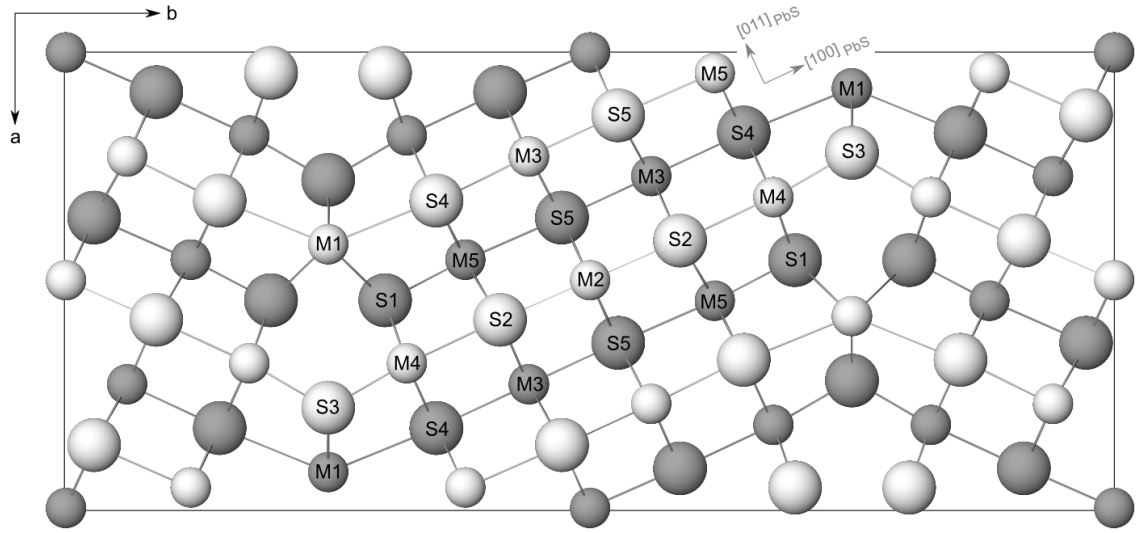

Figure 1: One unit cell from the crystal structure of heyrovskyite $Pb_6Bi_2S_9$ at ambient conditions. Gray circles represent atoms on the $z = 0$ mirror plane, white circles represent atoms on the $z = 0.5$ mirror plane. The orientation of the PbS-archetype axes inside one (010) structural slab is indicated.

A single-crystal of heyrovskyite was compressed in a diamond anvil cell and investigated with X-ray diffraction using a conventional laboratory X-ray source (a diffractometer IPDS-2T) in Bilbao. The crystal structure was found to be stable until at least 3.9 GPa and a new high pressure phase (β-$Pb_6Bi_2S_9$) was first observed at 4.84 GPa. The phase transition was clearly expressed by the appearance of a number of new reflections at $h/2$ k l of heyrovskyite accompanied by the change from a *B*-centred to a primitive lattice.

Although the data sets measured in the laboratory could well be used to determine the lattice parameters of β-$Pb_6Bi_2S_9$, they do not contain enough information about the reciprocal space (due to a relatively low energy of MoKα radiation of the laboratory diffractometer to determine the crystal structure. Therefore, one data set at 5.06 GPa has been measured using the marCCD-165 detector at the beamline D3 at the synchrotron HASYLAB, where a shorter wavelength of 0.4 Å was used. The data were integrated with the XDS program [2].

From the data set measured at D3, the crystal structure of β- $Pb_6Bi_2S_9$ has been solved and refined to the R(obs) factor of 8.17% in $Pna2_1$ ($Z = 8$). The unit cell has a volume of 3169.0(2.8) Å³ and contains 34 distinct atoms. This structure consists of two types of moduli with the SnS/TlI-archetype structure in which the Pb^{2+} and Bi^{3+} lone pairs are strongly expressed.

In addition to describing the crystal structure of β- $Pb_6Bi_2S_9$, the data set from HASYLAB allows us to describe the process of the phase transition in detail and compare the results to the closely related phase transition in lillianite [3,4].

References

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