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From lillianite to β-$Pb_3Bi_2S_6$: a crystal chemical study of $Pb_3Bi_2S_6$at high pressure

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A new high pressure phase in the group of sulfosalts has been found by using the diamond anvil cell technique combined with in-situ single-crystal X-ray diffraction. As pressure is applied to lillianite (Pb_3 Bi_2 S_6) a 1^{st} order phase transition is observed to take place between 3.7 and 4.9 GPa. It represents a rare example of a reconstructive and reversible transition where the crystal still diffracts as a single-crystal in spite of a dramatic structural change. The behaviour of lillianite is in contrast to previously studied sulfosalts that all were stable until at least 10 GPa. The crystal structure of the new phase (β-Pb_3Bi_2 S_6) is isotypic with meneghinite (Cu Pb_{13} Sb_7 S_{24}). The transition involves sliding between the layers of PbS archetype in lillianite to the SnS-like slabs in the meneghinite structure. The diamond anvil cell technique allows detailed crystal chemistry analysis on lillianite at various pressures as it is approaching the phase transition. Likewise, the ongoing evolution of β-Pb_3 Bi_2 S_6 has been followed until 10.5 GPa. Of special interest is the behaviour of the non-bonding electron pair in the valence shells of Pb and Bi. The stereochemical activity of the lone electron pairs is quantified by three-dimensional distortion parameters. The observed phase transition can contribute to the illumination of the poorly understood activity of the lone electron pairs and their influence on the stability of crystal structures.