

## High-pressure single-crystal synchrotron X-ray diffraction study of lillianite

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### ABSTRACT

In this paper, high-pressure data from a synchrotron X-ray diffraction study on a lillianite ( $\text{Pb}_3\text{Bi}_2\text{S}_6$ ) single crystal up to  $\sim 21$  GPa are presented. A phase transition from lillianite (space group  $Bbmm$ , LP lillianite) to the high-pressure form  $\beta\text{-Pb}_3\text{Bi}_2\text{S}_6$  (space group  $Pbnm$ , HP lillianite) was confirmed and bracketed between 4.90 and 4.92 GPa. The transition is reversible but of first-order with a hysteresis of  $\sim 2.8$  GPa. It showed weak effects of pseudo-merohedral twinning that disappeared upon decompression, testifying to a full recovery of the single crystal of lillianite. This makes lillianite an interesting shape-memory material.

With a bulk modulus  $K_{4.9} = 78(3)$  GPa and  $K' = 5.1(4)$ ,  $\beta\text{-Pb}_3\text{Bi}_2\text{S}_6$  is markedly less compressible than lillianite [ $K_0 = 44(2)$  GPa,  $K' = 7(1)$ ]. Compressional anisotropy increases markedly in  $\beta\text{-Pb}_3\text{Bi}_2\text{S}_6$  with compressibility along the  $b$  axis [ $M_{0b} = 130(6)$  GPa and  $M'_b = 19(3)$  in lillianite,  $M_{4.9b} = 145(4)$  GPa and  $M'_b = 16.0(7)$  in  $\beta\text{-Pb}_3\text{Bi}_2\text{S}_6$ ] significantly larger than that along the other two axes [ $M_{0a} = 118(5)$  GPa,  $M'_a = 21(3)$ ,  $M_{0c} = 139(12)$  GPa, and  $M'_c = 31(10)$  in lillianite,  $M_{4.9a} = 242(12)$  GPa,  $M'_a = 8(1)$ ,  $M_{4.9c} = 242(5)$  GPa, and  $M'_c = 29(1)$  in  $\beta\text{-Pb}_3\text{Bi}_2\text{S}_6$ ].

The behavior of lillianite at high pressure is an interesting case study in relation to non-quenched ultrahigh-pressure phases likely occurring in the inner Earth, like post-perovskite  $\text{MgSiO}_3$ , the oxide homologue  $N = 1$  of the lillianite series. The  $\beta\text{-Pb}_3\text{Bi}_2\text{S}_6$  structure, on the other hand, is the  $N = 3$  homologue of the meneghinite series to which the higher-pressure modification of the post-perovskite structure also belongs (homologue  $N = 1$ ). This makes the two forms of  $\text{Pb}_3\text{Bi}_2\text{S}_6$  potential equivalents of high- and ultrahigh-pressure Mg silicates that could occur both in the deep earth and in other rocky extrasolar planetary bodies.

**Keywords:** Lillianite, high-pressure, synchrotron, single-crystal X-ray diffraction, phase transition, shape-memory