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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 ($Pb_3Bi_2S_6$) single crystal up to ~21 GPa are presented. A phase transition from lillianite (space group *Bbmm*, LP lillianite) to the high-pressure form β-$Pb_3Bi_2S_6$ (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 ~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), β-$Pb_3Bi_2S_6$ is markedly less compressible than lillianite [K_0 = 44(2) GPa, K' = 7(1)]. Compressional anisotropy increases markedly in β-$Pb_3Bi_2S_6$ 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 β-$Pb_3Bi_2S_6$] 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 β-$Pb_3Bi_2S_6$].

The behavior of lillianite at high pressure is an interesting case study in relation to non-quenchable ultrahigh-pressure phases likely occurring in the inner Earth, like post-perovskite $MgSiO_3$, the oxide homologue N = 1 of the lillianite series. The β-$Pb_3Bi_2S_6$ 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 $Pb_3Bi_2S_6$ 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