# Incommensurate modulated crystal structure of lillianite-type $^4$L-$(Pb)_4(Cu,Sb)_8(Pb,Sb)_8Se_{24}$

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Incommensurate modulations in sulfosalt-like compounds might have been overlooked in the past due to their small deviation from commensurate superstructures.[1] These materials represent a large group of chalcogenides with a broad variety of sometimes complex crystal structures. As they contain only abundant elements, they represent interesting candidates for thermoelectirics. Synthetic $^4$L-$(Pb)_4(Cu,Sb)_8(Pb,Sb)_8Se_{24}$ obtained by melt synthesis from the elements crystallizes in the structure type of lillianite, $Pb_3Bi_2S_6$.[2] It can be described by tilted and distorted rocksalt-type slabs interconnected by cations in bicapped trigonal prims of Se atoms. The structure is classified as the $^4$L homologue as there are four edge-sharing octahedra across each NaCl-like slab.

After close inspection of the diffraction pattern, the crystal structure has been refined in the superspace group $Cmc2_1(\alpha 00)000$ with the modulation vector $q$ = 0.6882(3) $a^*$ with respect to the orthorhombic basic structure with $a$ = 4.165 Å, $b$ = 14.085 Å and $c$ = 19.82 Å. The exemplary cutout of the structure in Fig. 1 shows the slab that contains Sb/Cu and Pb/Sb mixed sites in an unusual sequence. The one-dimensional incommensurate modulation becomes evident from the coordination and therefore the position of the Cu atoms. While the mixed Pb/Sb sites are coordinated octahedrally by the Se atoms, approximately every third Pb/Sb position is replaced by Cu atoms that prefer a tetrahedral coordination of Se atoms. This phenomenon is a combination of a positional and occupational modulation that also affects Se-atom positions.

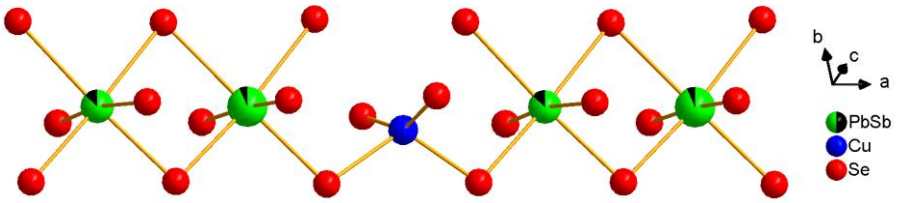


Fig. 1: Chemical nature of the modulation; almost every third Sb atom is replaced by a Cu atom

While single crystal X-ray diffraction at 120 K shows no significant change of the crystal structure, high-temperature measurements at 523 K reveal the disappearance of satellite reflections. This phenomenon is reversible and may be explained by a random distribution of the Cu atoms at high temperatures, where they share positions of the Pb/Sb site, so that long range order is no longer present.

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[2] Takagi J, Takéuchi Y. The crystal structure of lillianite. Acta Crystallogr. Sect. B, 28, 649-651 (1972),

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