A tunable structural family with ultralow thermal conductivity: copper deficient Cu1-xx Pb1-xBi1+xS3

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Résumé

Understanding the mechanism that connects heat transport with crystal structures and order/disorder phenomena is crucial to develop materials with ultra-low thermal conductivity, for thermoelectrics, and thermal barriers applications. We synthesized synthetic n-type bismuth-based sulfide mineral CuPbBi5S9 with ultra-low thermal conductivity (k) of 0.4-0.6 in the temperature range 300-700 K. By combining experiments and lattice dynamics calculations, we elucidated that the ultra-low k of CuPbBi5S9 is a result of combined structural disorder induced by the processing method and very low energy optical modes associated with Pb and Bi ions and, to a smaller extent, Cu. This vibrational complexity at low energy hints to a substantial anharmonic effect, reflected in a large Grüneisen parameter, that contributes to enhance phonon scattering. The drastic improvement of the carrier concentration and thermoelectric figure of merit upon Cl for S and Bi for Pb substitution highlights the ability of the Bi-S framework to generate n-type electrical conductivity. Our approach provides an interesting structural prototype for engineering n-type thermoelectrics chalcogenides by controlling disorder and optimizing doping.

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