Copper-containing sulfides as thermoelectric materials with low lattice thermal conductivities

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The discovery of cost-effective thermoelectric materials, containing abundant elements, is essential to enable widespread adoption of thermoelectric power generation. In this context, copper-containing sulfides are attracting considerable attention as alternative materials with promising thermoelectric performances, arising from their low thermal conductivities. Here, our recent work on a range of copper-containing sulfides, including tetrahedrite ($Cu_{12}Sb_4S_{13}$) and aikinite ($CuPbBiS_3$) will be presented, and the origin of their low thermal conductivities will be discussed.

Tetrahedrite is a promising *p*-type thermoelectric material with low lattice thermal conductivity (<1 W $m^{-1}K^{-1}$ at 300 K). Quasielastic neutron scattering (QENS) measurements, combined with molecular dynamics simulations, reveal that tetrahedrite behaves as an incipient ionic conductor, which is a material on the verge of ionic conduction, containing ions with appreciable mobility, but in which long-range ionic diffusion is suppressed due to the trapping effect of the underlying crystal structure. Analysis of inelastic neutron scattering (INS) data for tetrahedrite reveals the presence of a low-energy optical mode at 3-4 meV, which can be attributed to the confined diffusion of the copper ions. This low-energy optical mode, which softens on cooling revealing strong anharmonicity, is capable of strongly scattering the heat-carrying acoustic phonons, and hence significantly lowers the lattice thermal conductivity.

The lattice thermal conductivity of aikinite ($\kappa \approx 0.5$ W m^{-1} K^{-1} at 300 K) is close to the calculated minimum for amorphous and disordered solids. Sound velocity measurements reveal that the phonon mean-free-path is approximately 5 Å. Inelastic neutron scattering data unveil the presence of an anharmonic optical phonon mode at approximately 30 cm^{-1}, attributed mainly to the vibrations of the Pb^{2+} cations, and with an estimated lifetime of only 0.4 ps. Analysis of *ab-initio* molecular dynamics simulations shows that the Pb^{2+} lone pairs are rotating and that these rotations influence the Cu^{+} dynamics. The ultralow thermal conductivity of aikinite arises from the coupling of rotating Pb^{2+} lone pairs with the vibrational motion of the Cu^{+} cations.[2]

These findings unveil two new approaches for the design of materials with ultralow thermal conductivity, either by exploring systems in which incipient ionic conduction may be present or through the coupling of rotating lone pairs with vibrational motion.

References:

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[2] Carnevali, V., Mukherjee, S., Voneshen, D. J., Maji, K., Guilmeau, E., Powell, A.V., Vaqueiro, P., Fornari, M. Lone pair rotation and bond heterogeneity leading to ultralow thermal conductivity in aikinite**.** J. Am. Chem. Soc. 145(16), 9313–9325 (2023).