INSIGHTS INTO THE STRUCTURE-PROPERTY RELATIONSHIPS OF COPPER-CONTAINING THERMOELECTRIC SULFIDES

P. VAQUEIRO[a]

[a] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, UK*

p.vaqueiro@reading.ac.uk

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 several copper-containing sulfides, including tetrahedrite ($Cu_{12}Sb_4S_{13}$) and aikinite ($CuPbBiS_3$) will be presented, and the structural origin of their low thermal conductivities will be discussed.

Tetrahedrite is a promising *p*-type thermoelectric material with a low lattice thermal conductivity (<1 W $m^{-1}K^{-1}$ at 300 K), attributed to rattling vibrations of trigonal-planar copper ions. Analysis of neutron and synchrotron X-ray diffraction data shows that copper rattling is a direct consequence of a tetragonal-to-cubic phase transition at 90 K.[1] This phase transition occurs as a result of a Jahn-Teller electronic instability, which leads to the formation of "molecular-like" Cu_5^{7+} clusters and suppresses copper rattling vibrations below 90 K due to the strengthening of direct copper-copper interactions. Quasielastic neutron scattering (QENS) measurements, combined with molecular dynamics simulations, reveal that, above 200 K, 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.[2] 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. INS data reveal the presence of an anharmonic optical phonon mode at approximately 30 cm^{-1}, attributed mainly to the vibrations of the Pb^{2+} cations. Analysis of neutron diffraction data, together with *ab initio* molecular dynamics simulations, shows that the Pb^{2+} lone pairs are rotating and that, with increasing temperature, Cu^+ and Pb^{2+} cations, exhibit significantly larger displacements from their equilibrium positions than Bi^{3+} cations. The ultralow thermal conductivity of aikinite arises from the coupling of rotating Pb^{2+} lone pairs with the vibrational motion of the Cu^+ cations.[3]

[1] S. O. Long, A. V. Powell, S. Hull, F. Orlandi, C. C. Tang, A. R. Supka, M. Fornari and P. Vaqueiro *Adv. Funct. Mater.*, **2020**, 30, 1909409.
[2] S. Mukherjee, D. J. Voneshen, A. Duff, P. Goddard, A. V. Powell and P. Vaqueiro, *Adv. Mater.* **2023**, 35, 2306088.
[3] V. Carnevali, S. Mukherjee, D. J. Voneshen, K. Maji, E. Guilmeau, A. V. Powell, P. Vaqueiro and M. Fornari, *J. Am. Chem. Soc*., **2023**, 145, 9313.