Structural and thermoelectric properties of synthetic minerals: tetrahedrites and colusites

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As promising thermoelectric materials composed of environmentally friendly elements, copper-based chalcogenides have attracted increasing attention [1]. Examples are synthetic minerals of tetrahedrites and colusites, for which the combination of large Seebeck coefficient and low thermal conductivity leads to a high dimensionless figure of merit [2-6].

For the tetrahedrites $Cu_{12-x}Tr_xSb_4S_{13}$ (Tr: 3d transition metal), the suppressed lattice thermal conductivity has been attributed to the out of plane rattling of Cu atoms at a trigonal planer site [3,4,7]. Our investigations of the crystal structures and phonon dynamics of the tetrahedrites $Cu_{12}(Sb, As)_4S_{13}$ and $Cu_{10}Zn_2(Sb,As)_4S_{13}$ have revealed that the rattling of Cu atom originates from the chemical pressure inherent in the sulfur triangle [8]. Furthermore, this rattling vibration shakes neighboring metalloid atoms via assistance from the lone pairs of the metalloids, resulting in the low thermal conductivity.

The colusites $Cu_{26}A_2E_6S_{32}$(A=V, Nb, Ta; E=Ge, Sn) also exhibit low lattice thermal conductivity above 300 K [5,6]. We have studied the relationship between crystal structures and thermoelectric properties of colusites in comparison with tetrahedrites [9]. Because neither glass-like behavior nor rattling mode was found in the former, the low lattice thermal conductivity was attributed to the complexity of the lattice with a large number of atoms in the unit cell. Further investigation on the crystal structure of colusite revealed that atomic-scale defects/disordered states (interstitial defect, site splitting, and so on) are likely responsible for the reduced lattice thermal conductivity.

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