Long-range cationic order collapse triggered by S/Cl mixed-anion occupancy yields enhanced thermoelectric properties in Cu5Sn2S7

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Résumé

In this work, we investigated pathways to adjust the charge carrier concentration and optimise the thermoelectric performance of pristine and Cl-doped Cu5+ϵSn2-ϵS7. We characterised the structural properties, thermal stability and transport properties and demonstrated that Cl doping in Cu5Sn2S7-type monoclinic compounds induces a collapse of the long-range cationic ordering, ultimately leading to a sphalerite-type cubic phase characterised by ordered [SnS4]4 clusters. The change in crystal structure symmetry upon Cl doping was analysed by Rietveld refinements against X-ray powder diffraction data, transmission electron microscopy and low- and high-temperature transport properties measurements. The thermoelectric properties of the so-obtained cubic sphalerite Cu5+ϵSn2-ϵS7-yCly ($0 \leq \epsilon \leq 0.133$, y = 0.35, 0.70) are strongly enhanced with respect to the undoped Cu5Sn2S7: the power factor improves slightly while both electronic and lattice contributions to the thermal conductivity are reduced. Overall, single-phase Cl-doped Cu5.133Sn1.866S7-yCly ($y = 0.35$,

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0.70) compounds exhibit high thermoelectric performance, reaching a maximum ZT of 0.45 at 670 K.

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Mots-Clés: sulphide, disorder, mixed, anion