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Abstract

The Effects of Co-Doping Tetrahedrite with Ni and Se on the Thermoelectric Properties †

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One of the biggest obstacles to broadening the implementation of thermoelectric generators are the currently available thermoelectric materials, which tend to feature rare/expensive and toxic elements such as Bi, Pb or Te. In the pursuit of novel materials, researchers have been studying a p-type semiconductor mineral, named tetrahedrite ($Cu_{12}Sb_4S_{13}$). This mineral has low toxicity and is abundant in the surface of the Earth, displaying good electrical and thermal properties for thermoelectric applications, which led to a figure of merit, zT, of 0.6 at 700 K. Although current materials have higher performances (zT > 1.0), tetrahedrite has great potential for improvement via isovalent doping, as reported by various studies [1].

In this work, the effect in tetrahedrite thermoelectric properties of simultaneous isovalent doping of two elements, selenium (Se) and nickel (Ni), are presented. By employing Wien2K software [2] for calculating electrical band structures and density of states, coupled with BoltzTrap software [3], for calculating thermoelectric properties, simulations were conducted, which suggest that the optimum stoichiometric content for the highest thermoelectric performance (maximum zT), would be achieved with stoichiometric content of 0.5 Ni and 0.5 Se.

Thus, samples following the formula $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$ were produced and characterized by powder X-ray diffraction, Raman spectroscopy and scanning electron microscopy, with energy dispersive spectrometry. After annealing at 723 K for 7 days (the current stage in the production process), the samples display a major tetrahedrite phase, with the lowest estimated molar content being ≈84%, and a minor presence of secondary phases, mostly covellite and famatinite.

Measurements of the Seebeck coefficient and electrical resistivity not only indicate that co-doping improves the power factor, but they also are congruent with simulations, with the $Cu_{11.5}Ni_{0.5}Sb_4S_{12.5}Se_{0.5}$ sample achieving the highest power factor (1277.73 $\mu W/m \cdot K^2$ at 300 K). After estimating the thermal conductivity using the Wiedemann-Franz law and previously reported values for the lattice contribution, a figure of merit of zT = 0.32 at 300 K is obtained, which is one of the highest for this type of thermoelectric materials.

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