

Effect of substitutions in Fe/Ni/Sb skutterudite-type phases on thermoelectric properties

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Skutterudite-like compounds derived from CoSb_3 have been of great interest in the thermoelectric community because of their high electrical conductivities paired with high absolute Seebeck coefficients. Thermal conductivity can be decreased by introducing filling atoms into icosahedral voids of the structure. This combination makes these phases promising candidates for intermediate-temperature thermoelectrics. [1] Most skutterudite-like compounds crystallize in space group $Im\bar{3}$, a few anion coloring variants exhibit $R\bar{3}$. [2]

In this study, we investigated substitutions of skutterudites in the Fe-Ni-Sb system and the influence of additional elements on phase purity. Syntheses at 600-625 °C starting from FeSb_2 , NiSb_2 and Sb in fused silica ampules showed that only the nominal composition $\text{Fe}_{1.75}\text{Ni}_{2.25}\text{Sb}_{12}$ yields phase-pure samples with skutterudite-like structure. This is in contrast to older studies [3] claiming a compound $\text{Fe}_2\text{Ni}_2\text{Sb}_{12}$; however, our results concur with a more recent study on $\text{Fe}_{1.75}\text{Ni}_{2.25}\text{Sb}_{12}$. [4] The reason for this specific composition is not well understood; and the Fe/Ni distribution has to still be confirmed by e.g. resonant diffraction.

The icosahedral voids can be filled with Se and La. However, the ratio of Fe and Ni has to be adapted to the site occupancy of the filling atom. For every added Se atom, one Fe atom has to be exchanged for a Ni atom according to the formula $\text{Se}_x\text{Fe}_{1.75-x}\text{Ni}_{2.25+x}\text{Sb}_{12}$ with $x \lesssim 0.3$. For La, the higher the filling fraction of La, the more Fe is needed. On the Sb position, Sb can be substituted by Te and S. While for Te, the compositions follow the formula $\text{Fe}_{1.75+x}\text{Ni}_{2.25-x}\text{Sb}_{12-2x}\text{Te}_{2x}$ with x up to the maximum possible value of 2.25. For the S substitution, there is a competing reaction that affords FeS, which was not observed up to a nominal composition of $\text{Fe}_{2.05}\text{Ni}_{1.95}\text{Sb}_{11.7}\text{S}_{0.3}$. All of these compositions yield disordered skutterudites in $Im\bar{3}$.

The electrical conductivity of $\text{Fe}_{1.75}\text{Ni}_{2.25}\text{Sb}_{12}$ increases up to 690 S/cm at 723 K, indicating semiconducting behavior; the highest absolute Seebeck coefficient is $-84.5 \mu\text{V/K}$ at 523 K. The thermal conductivity decreases with higher temperatures down to 2.4 W/mK at 723 K, leading to a maximum thermoelectric figure of merit zT of 0.1 at 723 K. The substitution with S leads to a minimum in the thermal conductivity with 2.8 W/mK between 473 K and 573 K, moving the maximum figure of merit of 0.1 to 573 K for $\text{Fe}_{1.95}\text{Ni}_{2.05}\text{Sb}_{11.8}\text{S}_{0.2}$. In case of Te substitution, the lowest values are achieved at the lowest temperatures with 1.9 W/mK at 348 K, moving the maximum figure of merit into the 573 K to 673 K range for $\text{Fe}_2\text{Ni}_2\text{Sb}_{11.5}\text{Te}_{0.5}$.

The filling with Se increases electrical conductivity by a factor of 3, however, the thermal conductivity increases as well, with 4.0 W/mK at 348 K and 5.5 W/mK at 723 K. The highest absolute Seebeck coefficient is $-60.5 \mu\text{V/K}$ at 698 K where the highest figure of merit $zT = 0.08$ is found as well (values for $\text{Se}_{0.3}\text{Fe}_{1.45}\text{Ni}_{2.55}\text{Sb}_{12}$).

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[4] Artini, C., Fanciulli, C., Zanicchi, G., Costa, G. A., Carlini, R. (2017). *Intermetallics* **87**, 31-37.