Controlling the Figure of Merit in TiNiSn Half-Heusler Alloy: DFT Study

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TiNiSn half-Heusler (HH) alloys are considered as promising materials for application in thermoelectric devices. Improving their figure of merit may be achieved by increasing the Seebeck coefficient and/or by reduction of thermal conductivity. The magnitude of Seebeck coefficient depends on the shape of the electron Density of states (DOS) in the vicinity of Fermi energy, therefore engineering of DOS may improve thermoelectric figure of merit. Morphology of material influences the thermal conductivity, and this is an additional way to manage the thermoelectric efficiency. The promising method is to reduce the thermal conductivity by varying the average grain size in the sintering of nano-particles. The important question in this context is how the nanocrystalline structure influences their electronic properties. The aim of this presentation is to examine the improving thermoelectric figure of merit by Density Functional theory (DFT) calculations and statistical thermodynamics.

Investigation of different types of antisite defects shows that Ni antisite defects are more preferable energetically in comparison with other antisite defects. Influence of this defect on DOS is studied. Changes of DOS due to doping with iron and copper are presented pointing that alloying element may change the type of conductivity.

The analysis of the stability of TiNiSn with growing Ni contents is carried out for $T \neq 0$ by combining the DFT calculations with statistical thermodynamics. The approach bridges the gap between the quantum mechanical calculations of the phase stability in the ground state and the behavior of the alloys at elevated temperatures. The quasi-binary phase diagram beyond T=0K for TiNiSn-$TiNi_2Sn$ solid solutions is calculated with the energy parameters extracted from the calculations of the ordered structures on the Ni sublattice.

It is shown that the decomposition of the off-stoichiometric Ni-rich HH alloy in the stoichiometric phase and $TiNi_2Sn$ with the deficiency of Ni occurs at elevated temperatures – an effect which is confirmed by recent experimental data. Existence of the miscibility gap between TiNiSn and $TiNi_2Sn$ leads to phase separation in the nano-scale and to reduction of thermal conductivity recently found in experiments. It is discussed also how the formation of TiNiSn compound with grain boundaries may influence the conductivity of this material.