# Neutron Scattering Study on the Structure of $ZrNiSn_{1-x}Sb_x$ Bulk Thermoelectric Material

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**1. Introduction**

$ZrNiSn_{1-x}Sb_x$ is a group of promising thermoelectric materials due to its high power factor, which is attributed to the narrow band gap, sharp slope of the density of states near the Fermi level and simple crystal structure. However, the relatively high thermal conductivity hinders the further improvement on the thermoelectric performance. Different mechanisms have been employed to suppress the thermal conductivity, such as nanostructuralization, phase separation, nano-precipitates, hierarchical phonon scatterings and so on. In our previous experiment at J-PARC (project number: 2017A0118), it was interestingly found that there coexisted two phases with the same structure by different Ni contents. Occurrence of double phases in thermoelectric material is considered to be helpful for suppressing lattice thermal conductivity, hence improving thermoelectric performance. However, such phase separation is not reported in the ZrNiSn-based system previously. It is important and significant to study the details of the formation of double-phases and their exact influence on the transport properties of the ZrNiSn thermoelectrics. In this Fast Track Proposal, we studied the effect of heat treatment on the sample structures using the SuperHRPD instrument.

**2. Experiment**

Different from the samples used for the previous measurement, which were prepared by levitation melting without heat treatment (say as-prepared, AP, sample), the samples for the current experiment were processed using the spark pressure sintering method (say SPS sample). The measurements were taken on the BL08 SuperHRPD for ZrNiSn and $ZrNiSn_{0.88}Sb_{0.12}$. The NPD patterns were collected over the temperature range of ~10 K to ~300 K. Rietveld refinements were performed by the Z-Rietveld software. In the refinements, two phases, with the same crystal structure but different lattice parameters, different Ni concentration on the vacancy site and different atomic displacement parameters, were used.

**3. Results**

According to previous measurement, both AP-ZrNiSn and AP-$ZrNiSn_{0.88}Sb_{0.12}$ could be well fitted using two half Heusler (HH) phases. The process using spark plasma sintering leads to a single phase in the SPS-ZrNiSn sample, while double phases remains in the SPS-$ZrNiSn_{0.88}Sb_{0.12}$ sample. The double-phases here is attributed to the segregation of Ni interstitials, as demonstrated in Figs. 1(a). This moderate segregation of Ni interstitials here, nevertheless, does not lead to the emergence of full Heusler (FH) phase, rather two HH phases with different Ni concentrations and different lattice parameters (Fig. 1(c)). Theoretical calculation of the formation energy for ZrNiSn + xNi → $ZrNi_{1+x}Sn$ demonstrated a trend of moderate segregation of Ni interstitials in ZrNiSn

compound (Fig. 1(b)). The critical value locates around x = ~0.064, close to the experimental value of x = ~0.073 for the SPS samples (Figs. 1(a,b)). In addition, large part of the phase A transforms into the phase B after the SPS processing as shown in Fig. 1(d). This could be understood that the applied pressure during SPS favored the phase with smaller lattice parameters.

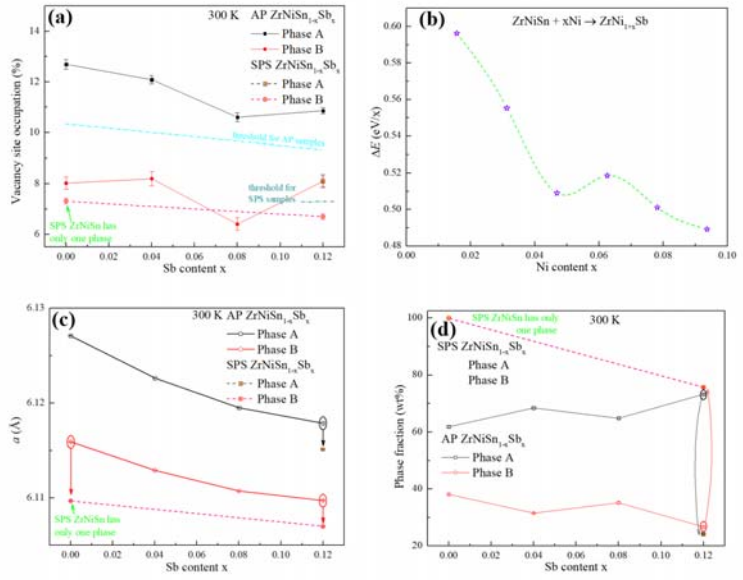


Fig. 1 (a) Ni concentration on the vacancy site of the phase A and phase B in AP and SPS $ZrNiSn_{1-x}Sb_x$ (x = 0, 0.04, 0.08 and 0.12) samples. (b) Calculated energy variations during the reaction from ZrNiSn + xNi to $ZrNi_{1+x}Sn$. Comparison of (c) lattice parameters and (d) the mass weighted phase fraction of the phase A and phase B in the AP- and SPS- $ZrNiSn_{1-x}Sb_x$ (x = 0, 0.04, 0.08 and 0.12) samples.

**4. Conclusion**

The experiment indicated that the heat treatment did have influence on the double-phases behaviors. The analysis of atomic mean-squared-displacement compared with the results from Phonon DOS measurement is ongoing. Preliminary analysis demonstrates that optical phonon might play an important role in the electrical transport properties. We hope the results could shed light on the understanding of the ZrNiSn-based materials.