

Experimental report

09/08/2024

Proposal: EASY-1132

Council: 10/2022

Title: In-situ study of the impact of excess Cu on phase formation of half-Heusler TiNiSn

Research area: Materials

This proposal is a new proposal

Main proposer: Jan Willem BOS

Experimental team:

Local contacts: Clemens RITTER

Samples: TiNiCu_{0.1}Sn

Instrument	Requested days	Allocated days	From	To
D20	12	12	24/08/2023	25/08/2023

Abstract:

The aim is to follow the formation of TiNiCu_{0.1}Sn from cold-pressed disks of mixed elemental powders. Sample to be heated at 3 deg/min to 900C (4-5 hr) and then left to anneal for 3-4 hours. D20 to use the ROC and blue furnace, wavelength 1.54 Å, $8 < d\text{-spacing} < 0.8 \text{ Å}$ to give best trade-off between flux and d-spacing range. This is sufficient to determine phase fractions. The scientific aim is to determine the impact of the excess Cu on the reaction pathway. From ex-situ work, we do not observe any full-Heusler phase (TiNi₂Sn) when using excess Cu. This is very different from the formation mechanism of TiNiSn, as recently published by us from in-situ NPD (Barczak et al. Chem Mater. DOI: 10.1021/acs.chemmater.3c00393). The proposed experiment will show if the FH phase is missing from the reaction path, or if there is a kinetic effect and it disappears more rapidly. Direct formation of the HH phase without interference of the FH would be of considerable interest for the design of TiNiSn-based thermoelectric materials. This experiment will provide key results for the PhD thesis for Mr Blair Kennedy, who is due to submit by September 2023, precluding a regular proposal.

Easy Access Report – Experiment 1132

“*In-situ study of the impact of excess Cu on phase formation of half-Heusler TiNiSn*”

This easy access experiment on the D20 instrument was performed with the purpose of investigating the formation mechanism of $\text{TiNiCu}_{0.1}\text{Sn}$ from its constituent elements. Elemental powders were cold pressed together in a suitable stoichiometric amount, before being loaded into the instrument in a Vanadium sample holder.

The system was then, under vacuum, heated at $3\text{ }^\circ\text{C} / \text{min}$ from room temperature to $900\text{ }^\circ\text{C}$, with NPD patterns taken every 150 seconds, roughly corresponding to 8 C steps. Excellent data quality was observed from the start of the experiment, see Figure 1(a), allowing the reaction mechanism to be followed. The first key step was seen at $231\text{ }^\circ\text{C}$, where elemental Sn melts and drives the formation of Ni-Sn binaries. After this, the observable system slowly loses Ni concentration, whilst the binary systems increase, and the Ti remains inert. As the system reaches $800\text{ }^\circ\text{C}$, the Ti suddenly reacts and the half-Heusler system is formed, becoming the majority phase by $900\text{ }^\circ\text{C}$.

The second step of this experiment involved a multi hour annealing step at $900\text{ }^\circ\text{C}$, wherein at the end of analysis the HH had become the major phase in the system, see Figure 1 (b). This relatively short synthesis time, in comparison to TiNiSn , drives the excellence of Cu as a dopant beyond optimising thermoelectric performance. Due to these findings, this work is intended to be published this year.

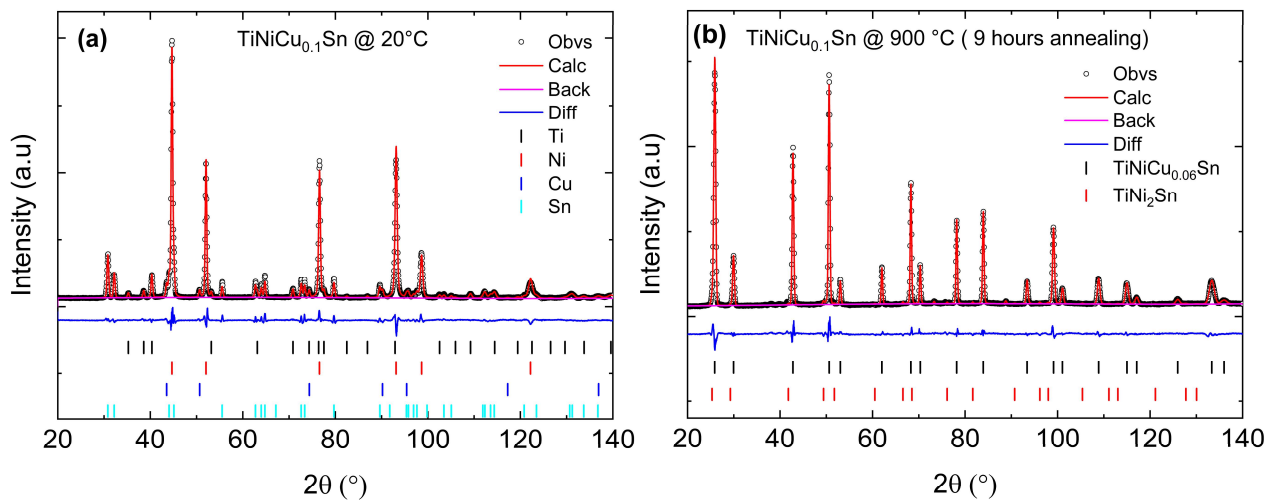


Figure 1 – NPD patterns and complementary Rietveld refinements for $\text{TiNiCu}_{0.1}\text{Sn}$ at (a) $20\text{ }^\circ\text{C}$ and (b) $900\text{ }^\circ\text{C}$ after 9 hours of annealing.