Understanding High Performance in Half-Heusler Thermoelectrics With Complementary Atom Probe Tomography and STEM-EELS

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Half-Heuslers are attractive as thermoelectric materials due to their mechanical strength, stability at high temperatures, cost and thermoelectric performance. In particular, TiNiSn based half-Heuslers offer an attractive balance between economic materials and commercially viable performance. Recent work has demonstrated that high performance from TiNiSn can be achieved by doping with trace Cu, simultaneously modulating the electronic carrier density and introducing phonon point scattering to lower lattice thermal conductivity (1). Addition of the Cu to TiNiSn has been demonstrated to modify the structure of the TiNiSn on many length scales, from the intergrain (10s μm) to the atomic (Å). In particular, it is vital to understand the distribution of trace Cu atoms at an atomic level, identifying any preferential site occupancies in the crystal lattice or local elemental concentration differences. In this work we demonstrate the advantages of a multi technique method that spans multiple length scales, combining the results from Atom Probe Tomography (APT) and high resolution Scanning Transmission Electron Microscopy (STEM). Our results are improved by sample preparation for APT using an Xe plasma focused ion beam (XE-PFIB) to minimise ion implantation and surface damage.

STEM combined EELS/EDX was used to provide structural and chemical information down to atomic resolution. For example, Figure 1 (a) shows a whole lamella and (b) EELS analysis across typical grain boundary showing Cu enrichment. While STEM offers much information on the sample, the technique is limited by its two-dimensional nature and difficulties with absolute quantification and detection of trace elements. APT is complementary in nature, since it is able to offer 3d reconstructions, absolute chemical concentration and quantify atoms at a few atomic percent along with their distribution, making it an ideal counterpart to STEM-EELS. An example of this is given in Figure 1 (b), which shows APT atom maps of major species detected across a grain boundary similar in nature to that in Figure 1 (b). The 3d nature of the grain boundary can be seen, along with absolute alloy concentrations for both grains and information on site-occupancy. APT shows the formation of intergrain oxide inclusions that are expected to modulate thermal transport in particular. Additionally, both techniques include a 'saturation' level of Cu doping, with excess Cu extruded to the grain boundary enhancing grain connectivity.

Our results help rationalise the structural and chemical reasons for the enhanced performance and are a critical step in the development of commercially viable thermoelectric generators. In addition, we demonstrate the importance of multiscale techniques.

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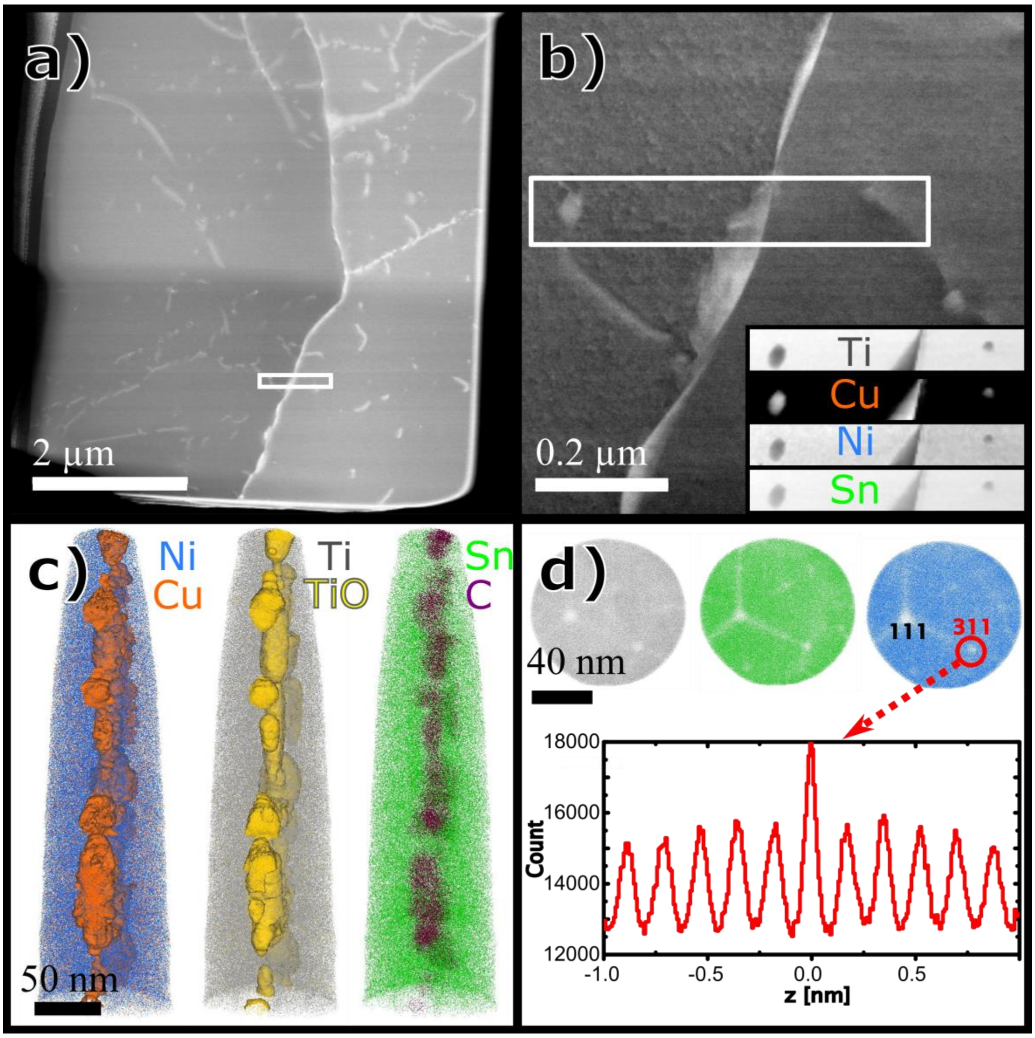

Figure 1 (a) Dark field STEM, highlighting grain boundaries and strain-inducing defects, (b) EELS analysis across typical grain boundary and spot-features, (c) APT atom maps of major species detected, each dot represents single atom field evaporated. Sample contains grain boundary running parallel to needle axis, (d) Sn-Ti Spatial distribution map showing site-occupancy behaviour of elements.