

Electron microscopy characterization of grain boundaries in Nb_{1-x}Ti_xFeSb based half-Heusler thermoelectric materials

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Background incl. aims

Thermoelectrics are a group of semiconductors which generate electrical power by conversion of heat into electrical energy. A thermoelectric power generator requires a hot and a cold side to use the temperature gradient for this conversion of energy. Microstructure engineering has been used in the thermoelectric material research community to reduce the phonon mean free path and thus led to reduction of thermal conductivity which is crucial for thermoelectrics. This can be done by grain refinement, i.e. reducing the grain size for more phonon scattering. The challenge remained to keep a high electrical conductivity since increasing the grain boundary fraction usually led to decrease of electrical conductivity. To achieve the desired properties in thermoelectrics, it is important to understand the dependence of the microstructure of grain boundaries and correlate it to the thermoelectric properties. For this, detailed electron microscopy investigations covering several length scales from the μm to an atomic scale need to be conducted.

Methods

Scanning electron microscopy (SEM) analysis including electron backscatter diffraction (EBSD) and energy-dispersive X-ray spectroscopy (EDX) has been done to observe the μm down to nm scale microstructure. The grain boundary characterization down to atomic scale was achieved with (scanning) transmission electron microscopy ((S)TEM). In addition, atom probe tomography (APT) was used to get a chemical analysis on the composition of the grain boundaries with highest accuracy and spatial resolution.

Results

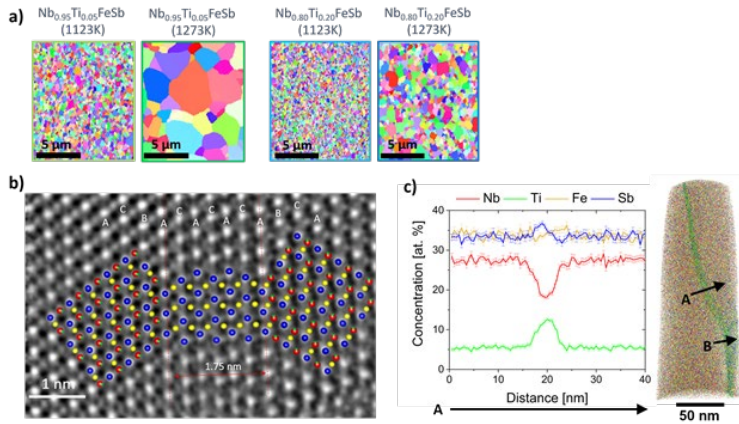
EBSD analysis of the grain size of the Nb_{1-x}Ti_xFeSb based half-Heusler thermoelectric materials synthesized at two different temperatures and two different Ti contents of 5% and 20% replacing Nb revealed a significant difference related to the grain size while all samples showed a random Mackenzie distribution for the grain misorientation (see Figure 1a). The later observation means that specific low angle grain boundary types were not dominating. To uncover this mystery and prove our hypothesis of resistive and conductive grain boundaries, we combined APT analysis with STEM analysis at the grain boundaries. We observed a defect grain boundary phase at random grain boundaries (Figure 1b) with chemical composition and lattice parameters differing from the one of the matrix phase of the half-Heusler material. The parameters are close to an FeSb phase in all four samples (different doping content and grain size) but with an additional segregation of Ti content for the high Ti doped samples which was shown with APT (see Figure 1c). This defect grain boundary phase proved to be the reason for increased electrical conductivity by providing conductive pathways in the high Ti doped sample.

Conclusion

Scale bridging electron microscopy was key to understand the correlation between microstructure and thermoelectric properties of NbFeSb based half-Heusler p-type

thermoelectric material.[1] We have revealed a way of decoupling the electrical and thermal conductivity to tune the properties for maximizing the materials performance. This way of grain boundary alloying will provide a new road map for microstructure engineering in the future and should also be applicable to other half-Heusler materials.

Graphic:



Keywords:

SEM, EBSD, STEM, APT, Thermoelectrics

Reference:

R. Bueno Villoro, D. Mattlat et al., Grain Boundary Phases in NbFeSb Half-Heusler Alloys: A New Avenue to Tune Transport Properties of Thermoelectric Materials, *Advanced Energy Materials*, 2204321, (2023)