The influence of Yb and Bi doping on the thermoelectric properties of Mg2Si0.4Sn0.6 studied using transmission electron microscopy

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Current research in thermoelectric materials is focused on increasing the figure of merit $ZT=(S^2\sigma/\kappa)T$ (where S is the Seebeck coefficient and σ is the electrical conductivity) by maximizing the power factor PF ($S^2\sigma$) and/or minimizing the thermal conductivity (κ). Attempts to maximize the PF include the development of new materials and optimization of existing materials by doping and nano-structuring. A reduction in thermal conductivity can be achieved by alloying, by producing disordered or complex unit cells or by nanostructuring. Here, we investigate a Bi-doped and a Bi- and Yb- doped $Mg_2Si_{0.4}Sn_{0.6}$ alloy. We discuss the influence of composition, crystal structure and microstructure on the thermoelectric performance of the materials, in order to assess new opportunities for enhancing the performance of bulk nano-structured composite materials.

Samples were produced by powder metallurgical processes, starting from a stoichiometric mixture of a melt-spun Mg or Mg-Yb pre-alloy and Si, Sn and Bi powders. After performing high energy milling to mix the components homogeneously under a protective Ar atmosphere, the material was simultaneously compacted and synthesized during a FAST process.

Pure $Mg_2Si_{0.4}Sn_{0.6}$ is an *n*-type semiconductor with a low value of σ. *S* is negative between room temperature and 600 °C. *σ* increases approximately linearly with Bi concentration. An optimized doping content leads to a value for *σ* of 140000-180000 S/m and a value for *S* of -150 µV/K at room temperature. Strong doping results in degeneracy of the semiconductor. Therefore, *σ* decreases with temperature, while *S* increases. The temperature dependence of *κ* shows two “branches”. In samples that have an optimized Bi doping concentration, *κ* decreases from room temperature to approximately 400 °C due to a dominant phonon-phonon scattering mechanism, with a minimum of 2 W/mK. At higher temperatures, thermal excitation of charge carriers across the band gap increases *κ*. Bi-Yb-doped $Mg_2Si_{0.4}Sn_{0.6}$ shows a larger ZT than the Yb-free sample.

We prepared specimens for high-resolution transmission electron microscopy (HRTEM) using an FEI Helios Nanolab 400s focused ion beam (FIB) dual-beam system. HRTEM images were acquired at 300 kV using an FEI Titan 80-300 TEM equipped with a spherical aberration (Cs) corrector on the objective lens. High-angle annular dark-field (HAADF) scanning TEM (STEM) images and elemental maps were acquired at 200 kV on an FEI Titan G2 80-200 TEM equipped with a Cs corrector on the condenser lens system.

An inspection of the microstructures of the materials by TEM reveals a homogeneous $Mg_2Si_{0.4}Sn_{0.6}$ matrix and a similar grain size distribution in both samples. The average grain sizes are in the range 1-3 µm, which shows that an improvement in the thermoelectric properties of the Bi- and Yb- doped alloy cannot be attributed to grain size. High spatial resolution energy-dispersive X-ray spectroscopy (EDXS) shows that the elemental distribution inside the grains differs from that at the grain boundaries. Our results show that Yb does not form a solid solution with $Mg_2Si_{0.4}Sn_{0.6}$, but instead forms distinct grains by reacting with Bi and Sn. The formation of Bi-rich precipitates in Bi- and Yb- doped $Mg_2Si_{0.4}Sn_{0.6}$ reduces the Bi content in the otherwise homogeneously doped matrix. Some oxygen enrichment in the region of the grain boundaries, associated with the formation of MgO and SiO_x, was observed in both samples. Sn and Si nanoscale precipitates were detected in the Bi-doped sample.

Acknowledgments:
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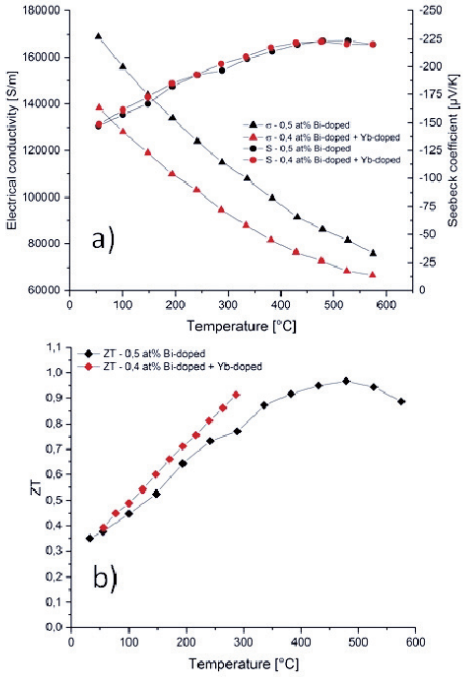

Figure 1. (a) Temperature-dependent electrical conductivity and Seebeck coefficient and (b) figure of merit for the Bi-doped and Bi- and Yb- doped samples.

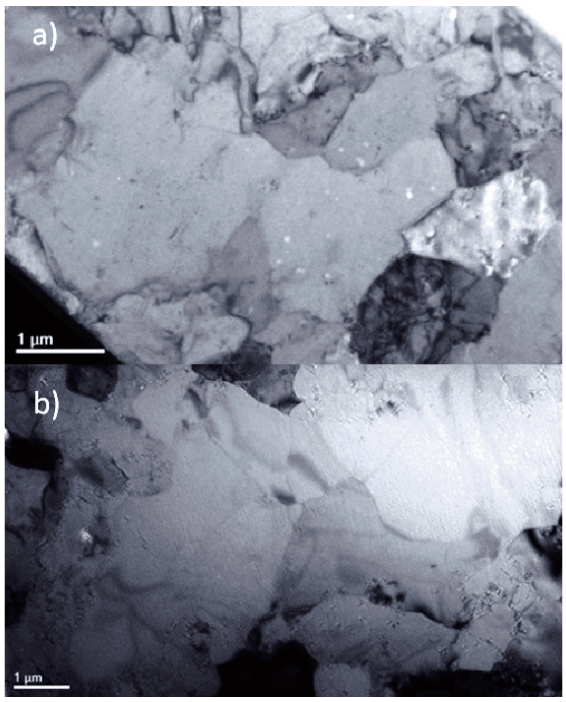

Figure 2 TEM images of sample (a) doped with Bi and sample (b) doped with Bi and Yb.

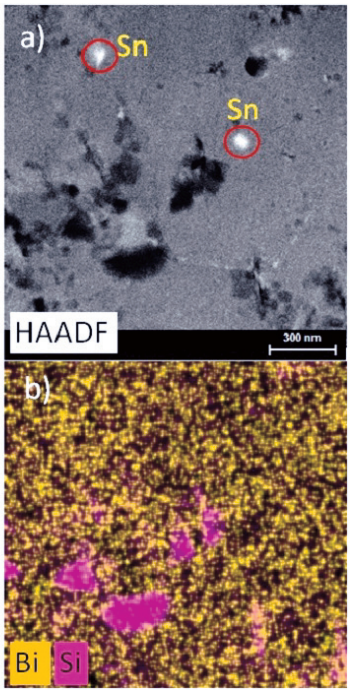

Figure 3. (a) HAADF image of the Bi-doped sample, with Sn-rich regions marked by red circles and b) EDXS elemental map recorded from the same area showing a homogenous distribution of Bi alongside Si precipitates.

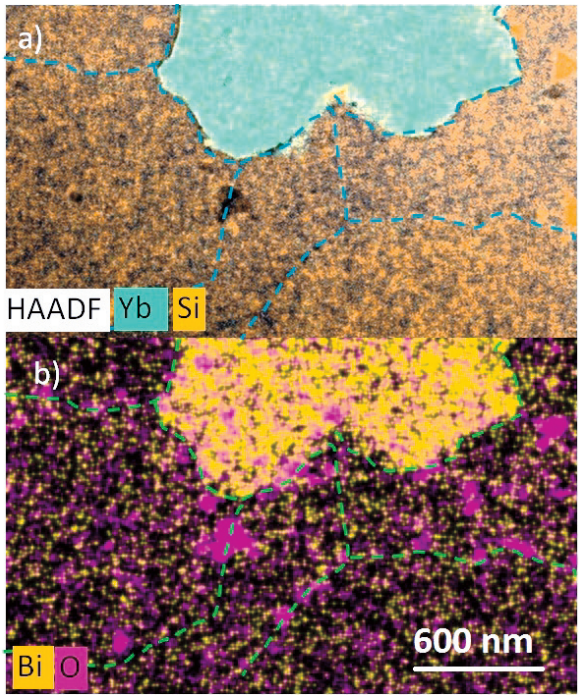

Figure 4. (a) HAADF image of the Bi- and Yb- doped sample, combined with an EDXS map of Yb and Si; b) EDXS elemental map recorded from the same area showing a homogeneous distribution of Bi in the matrix, Bi enrichment in Yb-Bi-Sn-precipitates and oxygen-rich particles (MgO). Dashed lines show the grain boundaries.