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TEM Characterization of a $Mg_2Si_{0.5}Sn_{0.5}$ Solid Solution for High-Performance Thermoelectrics

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Intermetallic compounds of Mg_2X (X = Si, Sn or Ge) are promising thermoelectric materials in the intermediate temperature range (400-800 K) because of their good electrical properties, low lattice thermal conductivity, and potentially high thermoelectric performance [1]. Studies have demonstrated that in the $Mg_2Si_{1-x}Sn_x$ system, $x \approx 0.5$ is one of the best choices for achieving a high thermoelectric performance of the material, because the large atomic mass difference between Si and Sn dramatically reduces the thermal conductivity of the solid solutions, which leads to a high value of figure of merit, *ZT*, of about 1.1 near 800 K [2]. The thermoelectric properties of these materials strongly depend on the local microstructure. Therefore, precisely understanding of the microstructure and composition of the material is essentially important for the development of high performance materials. In the present work, a $Mg_2Si_{0.5}Sn_{0.5}$ solid solution was characterized with TEM and other related methods, in scales from nanometer to sub-millimeter.

A $Mg_2Si_{0.5}Sn_{0.5}$ solid solution was prepared by mixing Mg_2Si and Mg_2Sn powders and hot-pressing the mixture [3]. The starting materials were powder of Mg (purity 99.9%), Si (99.9999%), and Sn (99.999%). Mg_2Si and Mg_2Sn alloys were synthesized by the liquid-solid reaction and the melting reaction methods, respectively. The obtained Mg_2Si and Mg_2Sn ingots were ground, mixed, and hot-pressed under Ar atmosphere at 80 MPa and 1068 K for 50 h. Structural and compositional characterization was carried out with XRD, SEM, electron probe microanalysis (EPMA), and TEM. The TEM observation and analysis were performed on a TEM, JEM-2100F (JEOL Co. Ltd.) operated at 200 kV. TEM specimens were prepared in two ways. One was the FIB method using a 30 keV Ga^+ ion beam (JEOL, JIB-4000). Another way was to crush bulk materials to powders in sub-micrometer size and load the powder on polymer microgrids.

XRD confirmed the successful synthesis of the $Mg_2Si_{0.5}Sn_{0.5}$ solid solution which was in an antifluorite structure. The samples exhibited a much lower thermal conductivity (1.92 W m^{-1} K^{-1} at 300 K) than the parent Mg_2Si (8.75 W m^{-1} K^{-1}) and Mg_2Sn compounds (6.28 W m^{-1} K^{-1}). The low thermal conductivity of $Mg_2Si_{0.5}Sn_{0.5}$ resulted in a relatively high $ZT = 0.0132$ at 300 K. SEM revealed that the grains were mainly 10-20 μm in size and had clean grain boundaries without obvious inclusions and precipitates. EPMA analysis at points and for elemental mappings revealed that the relative differences in composition between grains could reach several percents, and that there were differences in composition at grain boundaries and inside the grains. Figure1 shows the EPMA elemental mappings. TEM and STEM observations revealed that there were typical two kinds of grains, structurally homogeneous and heterogeneous ones. Almost no large inclusions were observed in the former grains, while inclusions of Si and Sn in size from tens to hundreds of nanometers were observed in the later grains. Futhermore, in both kinds of grains, high density MgO nanoparticles 10-20 nm in size were observed which dispersed evenly in the grains. Figure 2 shows the TEM images, and the selected area diffraction patterns (SADP)

of a specimen prepared with FIB from a homogeneous grain. When the specimen was observed in a direction out of a low index zone axis, diffraction rings were observed which were from tiny MgO particles. The bright dots observed in the dark field image were MgO nano particles which distributed evenly in the specimen. The Oxygen and/or MgO may be originated from the starting materials or the atmesphere during the synthesis process. Dispersed MgO nano particles could decrease the thermal concuctivity since they scatter phonons, therefore, they might be benifical to the thermoelectric performance of the material. The reasons for the MgO nano particles to distribute dispersely in grains may be that the alloing during the hot-press was processed partially in solid state. The existance of the unreacted Si and Sn inclusions and the heterogeneous in elemental distribution convinced that there is still a space to improve the thermoelectric performance of the materials by optimizing the synthesis procedure, alloy composition, and doping level, etc. [4]

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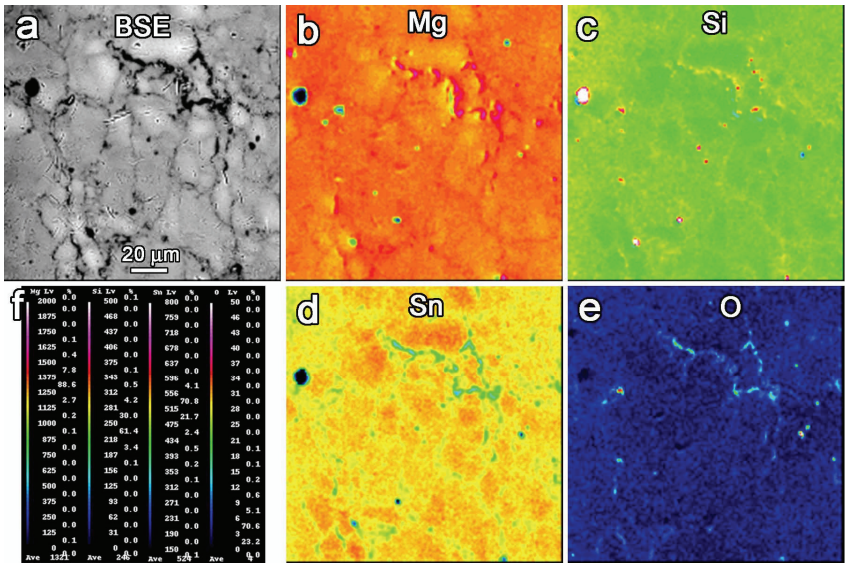

Figure 1. EPMA (electron probe microanalysis) elemental mappings of a $Mg_2Si_{0.5}Sn_{0.5}$ specimen. (a) Backscattered electron image; (b-e) Mappings of Mg, Si, Sn, and O, respectively; (f) Intensity scales of the mappings.

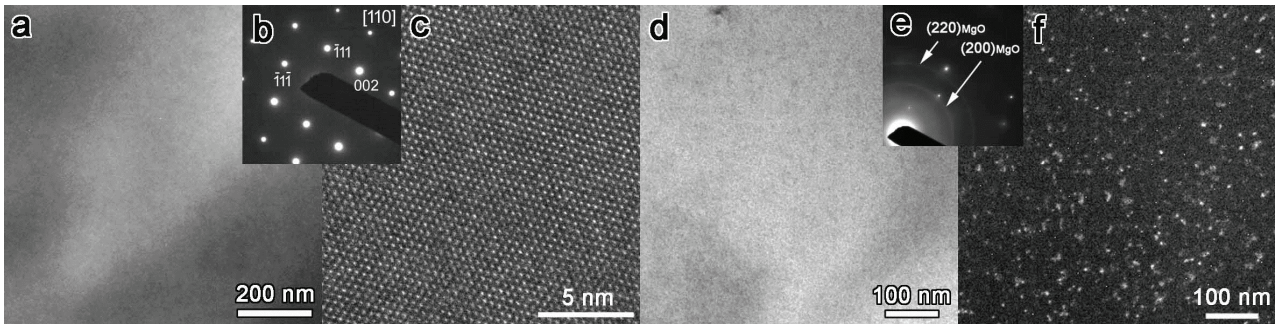

Figure 2. TEM images of a $Mg_2Si_{0.5}Sn_{0.5}$ specimen. (a-c) The BF (bright field), the SADP (selected area diffraction pattern), and high resolution transmission electron microscopy images observed in direction of [110]; (d-f) The BF, SADP, and dark field images observed in a direction out of a low index zone axis.

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