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Compositional Sensitivity of Microstructures and Thermoelectric Properties of $Ag_{1-x}Pb_{18}Sb_{1+y}Te_{20}$ Compounds

S. PERLT,[1,4] TH. HÖCHE,[2] J. DADDA,[3] E. MÜLLER,[3]
and B. RAUSCHENBACH[1]

1.—Leibniz Institute of Surface Modification, Permoserstr. 15, 04318 Leipzig, Germany. 2.—Fraunhofer Institute for Mechanics of Materials IWM, Walter-Hülse-Str. 1, 06120 Halle, Germany. 3.—German Aerospace Center, Institute of Materials Research, 51170 Köln, Germany. 4.—e-mail: susanne.perlt@iom-leipzig.de

This study reports microstructural investigations of $Ag_{1-x}Pb_{18}Sb_{1+y}Te_{20}$, i.e., Ag-deficient and Sb-excess lead-antimony-silver-tellurium-18 (LAST-18: $x \neq 0, y \neq 0$). Two different length scales are explored. The micrometer scale was evaluated by scanning electron microscopy (SEM) to analyze the number of secondary phases as well as composition. Site-specific focused ion-beam liftout of transmission electron microscopy (TEM) lamellae from thermoelectrically characterized samples was accomplished to investigate the structure on the nanometer scale. TEM was performed to reveal the shape and orientation relationship of nanoprecipitates. The study is completed with results for the thermoelectric properties for different values of x and y.

Key words: LAST, Microstructure analysis, Electron microscopy, Thermoelectricity, Secondary phases

INTRODUCTION

One feasible way to enhance the ZT value of a thermoelectric (TE) material is to decrease the thermal conductivity κ by introducing nanoscale precipitates that act as phonon scatterers. Therefore, precipitation of nanosized secondary phases in $Ag_{1-x}Pb_{18}Sb_{1+y}Te_{20}$ (lead-antimony-silver-tellurium, LAST) is highly promising for TE applications in the intermediate temperature range. The good thermoelectric performance of LAST—ZT values of ~2.2 at 800 K have been reported[1]—is, amongst other factors, assumed to be caused by nanoscale inclusions formed by nucleation and growth and/or spinodal decomposition.[2] In particular, LAST-18 compounds prove to have very good TE properties, caused by tuned amounts of Ag and Sb which form these nanoprecipitates as the Ag and Sb contents are above their respective room-temperature solubility limits in the PbTe matrix.[3] Materials processing plays a decisive role in adjusting TE properties. This applies particularly to the synthesis route, as there are deviating reports in literature on ZT values for LAST-18, ranging between 0.015[4] and 1.5[1] for different cooling rates of the melt. While the nanoprecipitates act as potential phonon scatterers decreasing the lattice thermal conductivity κ_L, the volume fraction of Sb and Ag and their ratio in the matrix also have a significant influence on the electronic properties of the material.[5] Based on TE properties monitored by a Seebeck scanning microprobe, structure–property relationships are studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. Site-specific liftout of TEM lamellae from thermoelectrically characterized samples is carried out by focused ion-beam (FIB) machining. Compositional analyses by energy-dispersive x-ray spectrometry (EDX) are combined with phase analyses via electron diffraction to give a detailed picture of the microstructure. In addition, high-resolution TEM is used to reveal the orientation relationships between the matrix phase and nanoprecipitates and their size distribution. Secondary phases are formed on the microscale during melt synthesis, with compositions being strongly influenced by the amounts of Ag and Sb in the material. On the nanoscale, TEM studies also reveal different morphologies of nanostructures such as plate-shaped Sb_2Te_3 precipitates.

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