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Effects of Microstructural Evolution on the Thermoelectric Properties of Spark-Plasma-Sintered $Ti_{0.3}Zr_{0.35}Hf_{0.35}NiSn$ Half-Heusler Compound

O. APPEL,[1,4] M. SCHWALL,[2] D. MOGILYANSKY,[1] M. KÖHNE,[3] B. BALKE,[2] and Y. GELBSTEIN[1]

1.—Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel. 2.—Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University, Mainz, Germany. 3.—Robert Bosch GmbH, 70049 Stuttgart, Germany. 4.—e-mail: oshratba@post.bgu.ac.il

The MNiSn (M = Ti, Zr, Hf) half-Heusler semiconducting compounds are widely investigated due to their good potential for thermoelectric (TE) power generation applications. In the current work, the evolution of the transport and structural properties of the $Ti_{0.3}Zr_{0.35}Hf_{0.35}NiSn$ compound upon various thermal treatments was studied. The nominal composition was arc melted, ball milled, and spark plasma sintered (SPS). Following SPS, large Hf-rich domains were found by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). Subsequently, the samples were subjected to homogenization treatments at 1163 K for 480 h and 610 h under argon atmosphere. Following these thermal treatments, the relative amount of the Hf-rich domains was reduced and they became smaller in size, with increasing thermal treatment duration. Nevertheless, no uniphased structure was reached. The dissolution of the Hf-rich domains in the half-Heusler matrix resulted in increase of both the Seebeck coefficient and electrical resistivity values and a decrease of the carrier concentration, attributed to elimination of these metallic domains. Resulting from the high atomic disorder caused by substitution at the M site, low thermal conductivity values of $\sim$3.8 W m^{-1} K^{-1} were obtained leading to high ZT values of up to 0.82 following SPS.

Key words: Half-Heusler, thermoelectrics, microstructure, efficiency figure of merit

INTRODUCTION

In recent years, interest in highly efficient thermoelectric (TE) materials has been continuously growing, due to the worldwide requirements to reduce greenhouse-gas emissions and global warming. Thermoelectric converters (TEC) are capable of direct conversion of residual heat generated by combustion engines, for instance, into electricity without the involvement of any moving parts. Thus, they not only decrease the reliance on fossil fuels but also actively reduce global warming effects.[1] TEC performance directly depends on the temperature gradient along the device, through the Carnot efficiency, and the intrinsic material properties, through the TE figure of merit (ZT), given by $ZT = \alpha^2 T/\kappa\rho$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature. TEC with high conversion efficiencies should possess high Seebeck coefficient, low electrical resistivity, and low thermal conductivity values and should operate over a broad temperature range.[2]

Current, state-of-the-art converters mainly contain tellurium-based TE compounds (e.g., PbTe and GeTe), which are too inefficient to be economic, due to both low efficiency values (5% to 10%) and expensive

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