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Synthesis and Measurement of the Thermoelectric Properties of Multiphase Composites: ZnSb Matrix with Zn_4Sb_3, Zn_3P_2, and Cu_5Zn_8

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We synthesized a series of samples with composition around 52 at.% zinc (Zn), 44 at.% antimony (Sb), 4 at.% phosphorus (P), and up to 3 at.% copper (Cu) by melting the elements and subsequent annealing. This resulted in dense and almost crack-free samples. X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) revealed composites with a majority phase of ZnSb containing varying amounts of Zn_3P_2 and Cu_5Zn_8, in addition to Zn_4Sb_3 in some of the samples. We measured the Seebeck coefficient, electrical conductivity, and thermal conductivity as a function of temperature. The thermoelectric performance tended to improve with increasing Cu content. At Cu content of 2 at.%, a reduced resistivity allows for the highest dimensionless figure of merit, with a maximum zT value of 0.18 at around 573 K.

Key words: Thermoelectric, ZnSb, microstructure, transport properties, figure of merit

INTRODUCTION

In a recent paper we demonstrated a thermoelectric figure of merit close to unity at around 550 K in ZnSb with P and Cu additives. This was achieved due to a reduced thermal conductivity and increased electrical conductivity.[1] The samples were synthesized by melting the elements, followed by quenching. Single-phase ZnSb is known to form cracks when cooled, so those samples were ball-milled and hot pressed. By ball-milling the samples, the grain sizes are reduced and the secondary phases are more uniformly distributed in the samples. In addition, defects might be introduced into the material by ball-milling. To achieve a high electrical conductivity it was found that the samples should have high density. However, high-density samples were difficult to achieve because that required hot pressing close to the melting temperature.

In this work we introduce excess Zn, in addition to P and Cu, in samples where ZnSb is the majority phase. This was motivated by the observation that cracking could be avoided by introducing excess Zn. With this less elaborate synthesis method, samples with high density were thus directly obtained from the solidified and annealed ingot.

For the development of thermoelectric technologies the identification of high-efficiency materials is essential. The thermoelectric efficiency is related to the dimensionless figure of merit,[2]

$$zT = \frac{S^2}{\rho(\kappa_e + \kappa_l)}T.$$

Here the Seebeck coefficient (S), electrical resistivity (ρ), and electronic thermal conductivity (κ_e) are intimately interrelated parameters.[3] The thermal conductivity, $\kappa = \kappa_e + \kappa_l$, has an electronic ($\kappa_e$) and a lattice ($\kappa_l$) contribution. In an ideal material, heat is carried as in a glass and charge carriers as in a crystal phonon glass electron crystal.[4]

Conventional thermoelectric materials are composed of toxic and/or rare elements. Devices based on Zn-Sb alloys are considered to be promising with respect to performance and environmental care.

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