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Thermoelectric properties of highly efficient Bi-doped $Mg_2Si_{1-x-y}Sn_xGe_y$ materials

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Abstract

In this work, Bi-doped $Mg_2Si_{1-x-y}Sn_xGe_y$ ($x = 0.4$ and $y = 0.05$) solid solutions with the nominal Bi content of $0 \leqslant z \leqslant 0.035$ were synthesized by solid state synthesis and sintering via hot pressing, and were studied in terms of structural, electronic transport and thermoelectric properties. These materials exhibit a high thermoelectric figure of merit, reaching a maximum of 1.4, which is the best among all reported $Mg_2Si_{1-x}Sn_x$ compounds on the Si-rich side. Within this range of Bi concentrations, X-ray diffraction, scanning electron microscopy and transmission electron microscopy characterization provided strong evidence for the presence of a number of secondary phases with different stoichiometries, including Si-rich, Sn-rich and Ge-rich phases. Moreover, the existence of micro- and nanofeatures is evident and their correlation with the thermoelectric properties and the high figure of merit is discussed. The influence of the amount of Bi doping on the thermoelectric properties of the specific compounds was investigated. A single effective mass was not proven efficient to fit the Seebeck coefficient and carrier concentration data, especially for carrier densities larger than 10^{20} cm^{-3}. The adopted synthesis process also yielded very good repeatability and regularity in obtaining enhanced thermoelectric properties.

Keywords: Thermoelectric; Silicides; High figure-of-merit; Bulk; Nanostructured

1. Introduction

As the global demand for energy increases, so does the demand for petroleum-, coal- and gas-based fuels that are currently consumed. However, over 60% of the energy released is lost as waste heat [1,2]. Therefore, the field of thermoelectric (TE) energy harvesting is rapidly advancing. The urgent need for renewable energy led, during the last decades, to intense scientific activity around energy efficiency and energy harvesting. Research and technology of advanced materials for TE applications and the design of new devices and structures has been noted since TE technology is directly related to energy systems [3]. Apart from the application of these materials to exploit waste heat, the direct conversion of solar thermal energy into electricity has also recently attracted particular interest [4]. Regarding the materials, the increasing demands of applications has led to a continuous search for improved materials in order to enhance TE performance. The TE efficiency is related to a dimensionless quantity, called the figure of merit (ZT), which comprises three key transport parameters [3]: the Seebeck coefficient, S, which expresses the ability of the material to generate a potential difference due to the applied temperature difference; the electrical conductivity, σ; and the thermal conductivity, κ, along with the absolute temperature T given by the expression $ZT = S^2\sigma T/\kappa$.

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The major research in the field of thermoelectrics has been focused on the increase of the Seebeck coefficient and the reduction of thermal conductivity, due to the interdependence of the three parameters S, σ and k in classical physics. The first generation of bulk thermoelectrics was developed over four decades ago with a ZT of ~0.8–1.0, and involved doped Bi_2Te_3 and PbTe bulk materials [3]. The next generation has focused on the development of new bulk materials based on the "phonon glass–electron crystal" concept (e.g. skutterudites [5], clathrates [6] and half-Heusler alloys [7]) and Zintl phases [8], and they have exhibited ZT values larger than 1. Among the primary methodologies in searching for thermoelectrics of the third generation, one approach is the nanostructuring of TE materials, which suggests that the ZT enhancement can be realized with nanoscale or nanostructured morphologies. Nanostructured materials have been theoretically predicted [9] to present considerably increased ZT and this has been also experimentally confirmed in the cases of both Bi_2Te_3/Sb_2Te_3 superlattices [10] (with ZT up to 2.4) and PbTe quantum dots (with $ZT = 2$ at 300 K) [11]. It has been also confirmed that nanostructured materials are more efficient compared to the conventional materials of the same stoichiometry [12–14]. Advances over the past decade show that it is possible to enhance ZT in nanoscale systems by using phonon scattering at interfaces [15] to reduce the thermal conductivity [16], and quantum confinement and carrier filtering [17–20] to enhance the power factor, $S^2\sigma$.

In the field of thermoelectrics, it is important to take sustainability into account since the overall ecological impact of using certain materials can be surprisingly high, especially for rare elements. Commonly used materials often contain rare elements such as Te and Bi; thus the likelihood of using them in a wider range of TE applications – particularly at levels that could impact global energy use – is uncertain. Silicide compounds seem to be a more advantageous choice, not only because of their ample availability in nature, but also because of their non-toxicity, consistent with the priority for environment- and human-friendly technology. Among silicide compounds, the Mg_2Si system seems to be the best, with the ternary series $Mg_2(Si,Sn)$ presenting high ZT, such as 1.1 for Sb-doped $Mg_2Si_{0.6}Sn_{0.4}$ [21,22], 1.3 for Sb-doped $Mg_2Si_{0.3}Sn_{0.7}$ [23] and 1.4 for Bi-doped $Mg_2Si_{0.4}Sn_{0.6}$ [24]. Although the Sn-rich side exhibits higher ZT values, the Si-rich side of the $Mg_2(Si,Sn)$ series seems to be more appropriate for applications due to the lower density, rather higher melting points and higher strength. Interestingly, quaternary $Mg_2(Si,Sn,Ge)$ systems have not attracted much attention apart from a few exceptions [25,26]. Very recently, a high figure of merit of this system was reported [27] where ZT reached 1.4 on the Bi-doped Si-rich $Mg_2Si_{1-x-y}Sn_xGe_y$ ($x = 0.4$, $y = 0.05$) material.

In this work, the full series of Bi-doped $Mg_2Si_{0.55}Sn_{0.4}Ge_{0.05}$ was studied in terms of structural features and TE properties. This series includes the material with a ZT of 1.4, which is the best out of all Si-rich $Mg_2Si_{1-x}Sn_x$ compounds, as presented in a short communication elsewhere [27]. Furthermore, the correlation of the structural micro- and nanofeatures with the TE properties and the high figure of merit is also discussed.

2. Experimental methods

2.1. Synthesis and sample preparation

Magnesium, silicon, tin, germanium and bismuth powders with purities higher than 99.8% (Alfa Aesar) were manipulated under argon in a dry glove box. The powders were mixed according to the $Mg_2Si_{1-x-y-z}Sn_xGe_yBi_z$ formula for $x = 0.4$, $y = 0.05$ and $0 \leqslant z \leqslant 0.035$. Mg excess of 10 mol.% was added to compensate for the magnesium loss during the heating steps. The samples were prepared in the following steps:

1- The powders were well mixed and cold-pressed. The pellets were sealed in quartz tubes under high vacuum and heated at temperatures up to 973 K to achieve partial reactivity. Graphite crucibles were used to avoid reaction with the quartz.
2- The obtained materials were subsequently ball-milled and were then cold-pressed again and heated at temperatures up to 973 K for 1 h.
3- Finally, the powders were uniaxially hot pressed under argon atmosphere at 1053 K temperature and 80 MPa pressure.

2.2. Structural characterization and elemental analysis

Powder X-ray diffraction (PXRD) patterns were obtained for all materials, using a Rigaku SmartLab System in order to (a) identify the phases, (b) evaluate the purity of the products and (c) estimate the corresponding lattice parameters. Rietveld analysis was performed using FullProf Suite software.

Scanning electron microscopy observations were carried out using a JEOL 840A. An attached energy dispersive spectrometer (Oxford, model ISIS 300) was used for energy dispersive X-ray analysis (EDX). The EDX mapping was performed in a JEOL scanning electron microscope (JSM-6610LV) and a Bruker Energy Dispersive X-ray spectrometer (QUANTAX 200).

Transmission electron microscopy (TEM) observations were carried out on selected samples using a JEOL 120CX electron microscope operating at 100 kV and a JEOL 2011 TEM operating at 200 kV and having a point resolution of 0.194 nm. Specimens suitable for electron microscopy observations were prepared by gluing crushed material on copper grids without any further process.