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High thermoelectric figure of merit of $Mg_2Si_{0.55}Sn_{0.4}Ge_{0.05}$ materials doped with Bi and Sb

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Thermoelectric properties of new Bi- and Sb-doped $Mg_2Si_{0.55}Sn_{0.4}Ge_{0.05}$ compounds prepared by powder methods were studied in the temperature range 300–823 K. The materials exhibited compositional inhomogeneites consisting of Sn-rich and Sn-poor areas. Doping with Bi or Sb had a very strong influence on the thermoelectric properties. A high figure of merit was obtained, with a value ~1.4 for Bi members and ~1.2 for Sb members at high temperatures. These values are the highest reported on this system.

Keywords: Thermoelectric materials; Silicides; Sintering; Mapping

The efficiency of a thermoelectric material is estimated by the so-called figure of merit (ZT), defined by the formula $ZT = \sigma S^2 T/\kappa$, where S is the Seebeck coefficient, T stands for temperature, σ represents electrical conductivity, and κ is the thermal conductivity. This formula is separated into two main parts: (i) σS^2, which is known as the power factor; and (ii) the thermal conductivity, where all these parameters are dependent on each other [1]. However, it is important to have a high power factor and a low thermal conductivity to achieve a high ZT, and this is already reported in various materials [2].

Mg_2Si-based materials are promising for thermoelectric conversion in the middle temperature range because of their attractive ZT, low density, low cost, non-toxicity and high abundance of constituents in the Earth's crust. In the 1960s, it was shown [3] that Mg_2X (X = Si, Ge, Sn) are promising candidates for thermoelectrics. Nikitin et al. [4] also presented partial phase diagrams of the $Mg_2(Si,Sn)$ pseudo-binary system, which present a miscibility gap, while Labotz et al. [5] reported a continuous formation of solid solution for $Mg_2(Si,Ge)$ series. $Mg_2(Si,Sn)$- and $Mg_2(Si,Ge)$-based thermoelectric materials have already shown a high ZT [6–13], but quaternary $Mg_2(Si,Sn,Ge)$ systems have not attracted much attention [14]. In Mg_2Si-based compounds, Sb and Bi are used as n-type dopants [6–13], and Li and Ag as p-type dopants [15].

Among the $Mg_2Si_{1-x}Sn_x$ series, the Sn-rich members (i.e., $x \geqslant 0.6$) exhibit high thermoelectric ZT when doped with Sb. The highest ZT achieved [10] for $Mg_2Si_{0.4}Sn_{0.6}$ was ~1.1 at 800 K. Extensive work has been done recently addressing the convergence of the conduction bands and the enhancement of the thermoelectric properties at $x = 0.65$–0.70 [9]. The member with $x = 0.6$ (i.e., $Mg_2Si_{0.4}Sn_{0.6}$) is situated in the boundary between the region of the formation of solid solutions and the miscibility gap that appears at Sn concentration of $0.4 \leqslant x \leqslant 0.6$. The $Mg_2Si_{1-x}Sn_x$ series, therefore, presents an unusual microstructure that seems to contribute to the best, up to now, ZT value of 1.3 [16].

This paper reports the synthesis and properties of a new compound based on the Si-rich-side $Mg_2(Si,Sn)$ series doped with Bi or Sb. This compound is situated on the other side of the miscibility gap ($Mg_2Si_{0.6}Sn_{0.4}$) compared with the compound studied in previous work ($Mg_2Si_{0.4}Sn_{0.6}$) [16]. In addition, a small amount of Ge was added, aimed at introducing additional atoms in the lattice, which may increase complexity in the system and affect the thermoelectric properties.

Samples were prepared by mixing the elemental powders with purity >99.9% (Alfa Johnson Matthey GmbH, Germany). The synthesis of the materials was carried out in three heating steps: The mixed powders were cold pressed and heated at temperatures up to 973 K to achieve partial reactivity. The materials obtained were subsequently ball-milled. The ball-milled powders were cold pressed again and annealed at temperatures up to

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973 K. Finally, the powders were uniaxially hot pressed under an argon atmosphere at 1043 K and 80 MPa pressure.

The samples were characterized by X-ray powder diffraction. The morphological characterization was carried out by scanning electron microscopy (SEM; Jeol) and energy dispersive X-ray spectrometry (EDX; Bruker). Thermal conductivity was measured by the laser flash technique at temperatures up to 823 K (LFA457, Netzsch). The electrical resistivity and Seebeck coefficient were measured simultaneously using ULVAC-ZEM3 for all the samples from room temperature up to 823 K.

Bi- and Sb-doped $Mg_2Si_{0.55}Sn_{0.4}Ge_{0.05}$ materials were synthesized for different x values in addition to $x = 0$. The x_{Bi} values were 0.0175 and 0.02 for Bi members, and the x_{Sb} values were 0.0075 and 0.0125 for Sb members.

X-ray powder diffraction of all the samples was performed, and Figure 1 shows typical patterns of the material after each heating step for the Sb-doped member ($Mg_2Si_{0.55-x}Sn_{0.4}Ge_{0.05}Sb_x$, $x = 0.0125$). It is clear that, during the first heating, most of the starting materials have reacted, and only a very small amount of residuals exists. The major phase is that of Mg_2(Si,Sn,Ge), but there is not a single composition, as concluded from the wide/split peaks that correspond to this phase. After the second heating step, the Mg_2(Si,Sn,Ge) phase peaks are less wide/split, suggesting better mixing and the formation of a more homogeneous material that corresponds to a narrower composition range. Finally, after the third heating step (hot pressing), the peaks are even narrower and closer to the composition of $Mg_2Si_{0.6}Sn_{0.4}$. Although the main phase was always of the CaF_2-type, a small amount of MgO was observed in all samples. Many research groups working with Mg_2Si-based thermoelectric materials have already reported the presence of MgO in their samples [6,7,13,17].

In order to study the morphology of the $Mg_2Si_{0.55}Sn_{0.4}Ge_{0.05}$ materials, the hot pressed samples were examined by SEM/EDX (see Fig. 2). Based on the backscattered images, it is clear that the material presents compositional inhomogeneities. Owing to these compositional variations, EDX mapping was carried out for the different elements, i.e., Si, Sn and Ge. Figure 2b, c and d shows the distribution of Si, Sn and Ge, respectively. It is observed that there are Sn-poor (Si-rich) and Sn-rich (Si-poor) areas. These areas correspond to darker and brighter regions in the backscattered image, respectively. Where Si is more evident,

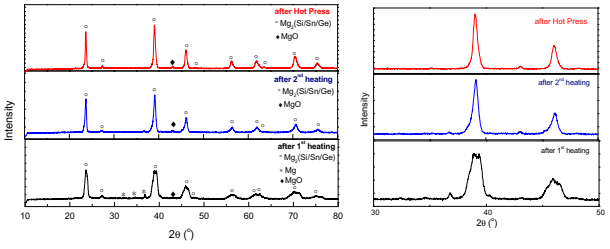

Figure 1. XRD patterns of $Mg_2Si_{0.55-x}Sn_{0.4}Ge_{0.05}Sb_x$ ($x = 0.0125$) material after each heating step during synthesis.

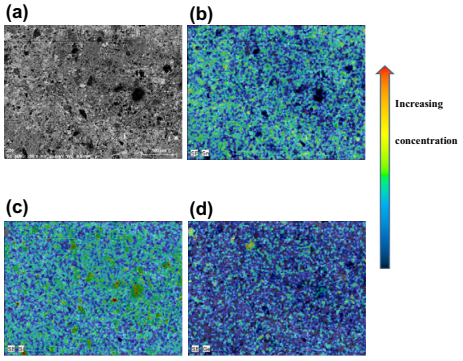

Figure 2. Backscattered SEM image of the hot-pressed $Mg_2Si_{0.55-x}Sn_{0.4}Ge_{0.05}Sb_x$, $x_{Sb} = 0.0125$, material and the elemental mapping images of (b) Sn, (c) Si and (d) Ge. The colors are qualitatively adjusted based on the concentration of each element separately.

less Sn exists, and this behavior is also evident in the Sn-rich members [16] of the $Mg_2Si_{1-x}Sn_x$ series (i.e., $x = 0.6$), where a Si-rich second phase as well as the complementary Si/Sn mapping is also observed. Ge distribution seems to be more uniform, although Ge-rich inclusions also exist. All these inclusions enhance the inhomogeneities and complexity of the microstructure and may affect the properties.

The electrical resistivity and Seebeck coefficient were simultaneously measured at temperatures up to 823 K (see Fig. 3a and b). The Seebeck coefficient was negative throughout the investigated temperature range, showing the n-type character of these materials, as expected from the $Si^{+4}/(Bi,Sb)^{+3}$ substitution. When the Bi concentration increases, the Seebeck coefficient decreases (absolute values) from $-395\ \mu V\ K^{-1}$ for $x_{Bi} = 0$ to $-94\ \mu V\ K^{-1}$ for $x_{Bi} = 0.0175$ and $x_{Bi} = 0.02$. For Sb members, the Seebeck coefficient decreased again from $-395\ \mu V\ K^{-1}$ for $x_{Sb} = 0$ to $-133\ \mu V\ K^{-1}$ for $x_{Sb} = 0.0075$ and to $\sim -105\ \mu V\ K^{-1}$ for $x_{Sb} = 0.0125$ at room temperature. Moreover, the temperature dependence of all doped (Bi/Sb containing) materials is different compared with the undoped materials, owing to their higher doping level (i.e., higher carrier concentration). For the undoped material, the Seebeck coefficient increases initially, but soon reaches its maximum at 150 °C and then starts decreasing (see Fig. 3a), in agreement with the literature [14]. The Seebeck coefficient values are similar to those [9,10] of $Mg_2Si_{1-x}Sn_x$ for $x = 0.4$.

In contrast, the electrical conductivity of the undoped material ($x = 0$) is low and increases with temperature, which is typical behavior for this semiconducting compound (see Fig. 3b). Doping has a significant influence on the electrical conductivity, and even a very low amount of dopant ($x_{Sb} = 0.0075$) changes the temperature dependence as a result of the increase in carrier concentration, in agreement with the Seebeck coefficient data. Moreover, the electrical conductivity increases with increasing Bi/Sb concentration. The temperature dependence for the Bi/Sb-containing materials is in agreement with the highly doped semiconductors. The highest electrical conductivity obtained in the present