Microstructure Investigations of Yb- and Bi-doped Mg₂Si Prepared from Metal Hydrides for Thermoelectric Applications

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ABSTRACT

Within the field of thermoelectric materials for energy conversion magnesium silicide, Mg_2Si , is an outstanding candidate due to its low density, abundant constituents and low toxicity. However electronic and thermal tuning of the material is a required necessity to improve its Figure of Merit, zT . Doping of Yb via reactive YbH_2 into the structure is performed with the goal of reducing the thermal conductivity. Hydrogen is released as a by-product at high temperature allowing for facile incorporation of Yb into the structure. We report on the properties of Yb- and Bi-doped Mg_2Si prepared with MgH_2 and YbH_2 with the focus on the synthetic conditions, and samples' microstructure, investigated by various electron microscopy techniques. Yb is found in the form of both Yb_3Si_5 inclusions and Yb dopant segregated at the grain boundary substituting for Mg. The addition of 1 at.% Yb concentration reduced the thermal conductivity, providing a value of $30 \text{ mW/cm}\cdot\text{K}$ at 800 K. In order to adjust carrier concentration, the sample is additionally doped with Bi. The impact of the microstructure on the transport properties of the obtained material is studied. Ideally, the reduction of the thermal conductivity is achieved by doping with Yb and the electronic transport is adjusted by doping with Bi. Large grain microstructure facilitates the electronic transport. However, the synthetic conditions that provide the optimized microstructure for electrical transport do not facilitate the additional Yb dopant incorporation. Therefore, the Yb and Bi containing sample with the optimized microstructure provides a $zT = 0.46$ at 800 K.

KEYWORDS

Magnesium silicide, Thermoelectric Materials, Ytterbium, Bismuth

1. Introduction

First studies on the thermoelectric properties of Zintl phases of the composition Mg_2X ($\text{X} = \text{Si, Ge, Sn}$) and their solid solutions were made about 50 years ago [1, 2]. These investigations showed their promising potential for thermoelectric applications, because of the large Seebeck coefficients, low electrical resistivity, along with thermal stability, environmentally friendly elements with relative abundance and low density. Research on these materials has recently significantly increased because they are considered to be high-performance thermoelectric materials between 500 K and 900 K, which can convert wasted heat produced by functioning automobile exhaust into useful electricity [1-4].

Mg_2Si needs modifications to obtain good thermoelectric properties, such as reduction of the lattice conductivity and increase in carrier mobility. In order to decrease the thermal conductivity several ideas have been discussed in literature. One is to replace the Mg^{2+} in the crystal structure of Mg_2Si by a heavier element. This will introduce disorder into the crystal lattice affecting scattering of heat carrying phonons, thus reducing thermal conductivity. *Meng* et al. have shown that this is possible with yttrium, Y [5], and *Todaka* et al. published thermoelectric data on sodium, Na, -doped Mg_2Si [6]. In these examples the divalent Mg-cation is replaced by either a trivalent or monovalent cation, which leads to defects in the crystal structure and consequently affecting the carrier concentration. Therefore it is not possible to isolate the effect of the substituting element. To avoid this problem, *Zhao* and coworkers showed that the substitution of Mg^{2+} with isovalent Ca^{2+} is possible according to $\text{Mg}_{2-x}\text{Ca}_x\text{Si}$ with x up to 0.1 [7]. Since the thermal conductivity is related to the scattering of the phonons by crystal lattice vibrations, heavier elements should be more effective scattering centers and therefore reduce the phonon mean free path more efficiently.

Two other approaches to lower thermal conductivity are to make nanocrystalline Mg_2Si [8] or to incorporate nanoparticles to form composite materials [10]. *Mingo* and co-workers have shown with calculations on thermal conductivity that metal silicide nanoparticles have a significant influence when doped into $\text{Si}_{1-x}\text{Ge}_x$ alloys [9]. Silicon nanoparticles for example have been experimentally shown to affect the thermal conductivity by reducing the phonon mean free path in Mg_2Si [10]. This has been also found to be true for $\text{Mg}_2\text{Si}_x\text{Ge}_y\text{Sn}_{1-x-y}$ [11].

In addition to reducing the thermal conductivity in Mg_2Si , the electrical transport also needs to be adjusted. The optimization of charge carrier concentration can be achieved by doping Mg_2Si with group 15th elements, such as Sb or Bi [12-15]. These dopants have a combined effect on the material, since doping with these heavy elements increases the scattering of heat carrying phonons due to point defect scattering and at the same time add

excess electrons, which affects the carrier concentration. For plain Mg_2Si , Bi doping has shown the best results to date with $zT \sim 0.7$ at 775 K [15-19].

The reactive spark plasma sintering (SPS) of the magnesium hydride and doped silicon was shown to be facile route for the one-step preparation and densification of Mg_2Si -based materials [10]. The process facilitates preparation of the oxide-free magnesium silicide products with high density [8, 10, 20]. Herein, we present the effect of Yb and Bi doping into Mg_2Si via a MgH_2 route and the microstructure study of as a function of the sintering temperature in order to provide a better understanding of the dopant and microstructure-property relationship. Addition of YbH_2 to the synthetic route is used to further reduce thermal conductivity. There are two results of the addition of YbH_2 . The first is the isovalent substitution of Mg^{2+} by heavier Yb^{2+} and the second is the formation of a Yb-containing precipitate in the Mg_2Si matrix. Bi dopant is employed to control the transport properties. The microstructure is studied as a function of ball milling and sintering temperature. The resulting composite phase is characterized and the impact of dopant and microstructure on the thermoelectric properties is discussed.

2. Results and Discussion

2.1. Synthesis

Thermogravimetry / differential scanning calorimetry (TG/DSC) investigations indicated that this reaction proceeds in the manner described according to reaction (1). (See Supporting Information)

The results are similar to those previously reported [10] and in good agreement with the reported decomposition temperatures of MgH_2 : 652 K in Spark Plasma Sintering (SPS) process and 667 K in DSC [20, 21]. The endothermic peak with its onset at 671 K is close to 680 K determined in the detailed studies regarding the reaction kinetics in the Mg-Si-H system [22]. Similar to previous reports [10][22], the mass loss is lower than the expected loss of hydrogen (5 wt-%) based on the reaction equation. Reaction kinetics [22] show that activation rates are strongly correlated with particle size. The reaction does not take place in the the ball milling step [22]; in contrast to the mechanical alloying of Si with magnesium metal to form Mg_2Si [17, 20].

The ball milled powders of MgH_2 , Si and the respective Bi and/or YbH_2 dopants were sintered and reacted in a single step using the SPS technique. The ball-mill time varies and is

denoted as *short* for two sets of 30 minutes or *long* for 9 hours of ball-milling in 15 minute on/off intervals (see experimental and Table 1). The *long* ball-milling time is slightly shorter than that previously reported [8, 10], but was deemed sufficient based on the resulting powder X-ray diffraction of the SPS powder. The *short* ball-milling was determined by powder X-ray diffraction to also be sufficient for producing nearly phase pure Mg_2Si . The sintering temperature was investigated as well and Table 1 provides the details for each sample. The maximum temperature of 1023 K was chosen as the highest possible to apply without significant loss of Mg.

Table 1: Synthetic conditions used to obtain the samples discussed herein.

ID	Yb (at.-%)	Bi (at.-%)	ball milling‡	temperature(K)	density,%
I	1.0	–	short	973	98%
II	0.5	–	short	973	97%
III	0.2	–	short	973	100%
IV	1.0	1.0	long	773	98%
V	1.0	1.0	long	923	95%
VI	1.0	1.0	long	1023	99%
VII	–	1.0	short	973	98%
VIII	0.2	1.0	short	973	97%

‡ *short* = two sets of 30 minutes; *long* = 9 hours of 15 minute on/off intervals

2.2. Lowering thermal conductivity with YbH_2 – proof of concept and optimization

In order to investigate the effect of Yb, either as a dopant or alloy, on the thermoelectric properties, three samples with different Yb dopant concentrations (0.2%, 0.5% and 1.0% (I-III)) were prepared via a *short ball-milling* approach (Table 1). Short ball-milling was explored as it has been shown that nanopowders of Si can be problematic for forming dense pellets [20]. Stoichiometric amounts of MgH_2 , YbH_2 and Si along with the dopants were ball-milled and loaded into graphite dies. The reactants were handled as described in the experimental section (*vide infra*) and sintered in the SPS as described above. The obtained samples were investigated by powder X-ray diffraction and showed Mg_2Si and a small amount of Si. No peak broadening was observed, indicating that the material particle size after SPS is ≥ 100 μm . Yb_3Si_5 was observed in the samples with 1% of Yb prepared via *long* ball-milling and in the sample VIII prepared via *short* ball-milling. No other ytterbium silicides were identified. Within the error of the measurement and the absence of an internal standard, no change of the lattice parameters was observed. The X-ray powder diffraction patterns of all samples are provided in the Supporting Information (Fig. S2-S9).

To obtain more information about the elemental distribution within the pressed pellets, a 1% Yb containing Mg_2Si sample (I) was investigated using electron microprobe analysis. X-ray mapping was used to display the elemental distribution within an area of $200 \times 200 \mu\text{m}^2$ (Fig. 1). As seen from the X-ray maps, Mg poor areas contain excess Si. Electron microprobe analyses showed the expected composition of the matrix, the determined doping levels were close to the experimentally used concentrations. For Yb, low counts can be seen across the whole sample, which gives rise to the assumption that Yb^{2+} was alloyed into Mg_2Si , along with bright spots, which can be attributed to the Yb_3Si_5 phase identified by powder X-ray diffraction.

Figure 1: Back scattering electron image (top left) and elemental maps of Mg (top right), Si (bottom left) and Yb (bottom right) of a 1% Yb doped Mg_2Si sample (I).

In addition scanning transmission electron microscopy (STEM) was applied to image both the Yb_3Si_5 inclusions and the microstructure of the 1% Yb containing sample (I). Atomic number Z-contrast image, an incoherent imaging that is sensitive to the atomic number, can be obtained by collecting the diffracted electrons in the dark field using a high angle annular dark field (HAADF) detector. Energy dispersive X-ray spectroscopy (EDX) analysis can be performed alongside the Z-contrast imaging. Figure 2 (*top*) shows a HAADF imaging of the Yb_3Si_5 inclusion embedded in the Mg_2Si matrix. The inset image shows the whole Mg_2Si particle where the magnified image was acquired. The particles with a bright contrast were identified as the Yb_3Si_5 phase. The *bottom* graph shows the energy dispersive X-ray spectroscopy (EDX) data taken from the inclusions to verify the presence of Yb. Atomic

resolution STEM-HAADF imaging was applied to identify the Yb distribution at the Mg_2Si grain boundary. Figure 2a shows the Yb segregation along the grain boundary of Mg_2Si . Figure 2b at higher magnification shows the atomic columns of Si (marked by the red lines) and Mg (between the solid lines). Since all the Yb dopants with bright contrast fall between the lines one can conclude that Yb substitutes for Mg in Mg_2Si instead of Si. Therefore Yb plays two roles in Mg_2Si : it distributes as Yb_3Si_5 precipitates and at the grain boundaries substituting for Mg according to $\text{Mg}_{2-x}\text{Yb}_x\text{Si}$. Observations of the formation of Mg containing phases (Mg_3Sb_2 and Mg_3Bi_2) at the grain boundary have been made by Farahi and coworkers in the investigation of Sb- and Bi-doped Mg_2Si [15].

Figure 2: STEM image of a Mg₂Si particle with Yb₃Si₅ inclusions (a). The inclusions have a size of about 40 nm. *Inset* shows the whole particle of Mg₂Si. EDX was acquired from the same specimen area as shown in the STEM image. The presence of Yb as well as Mg, Si and O are clearly identified in the EDX spectrum. The Cu peaks visible are due to the specimen grid used. HAADF-STEM images of a Yb-doped Mg₂Si sample showing Yb segregation along the grain boundary (b). The higher magnification image in (c) reveals that the Yb dopants (bright contrast) do not occupy the Si columns (marked by the line). The Mg columns are located between the lines with a slightly darker contrast than that of Si. The images were high-pass filtered to reduce the high frequency scanning noise.

The thermal conductivity was calculated from the measured thermal diffusivity (α), the measured geometrical density (ρ) and the specific heat capacity (C_p) using the following equation: $\kappa_{\text{total}} = d \cdot C_p \cdot \alpha$. For the specific heat capacity C_p values published in an earlier report were used [23]. Figure 3 shows the total thermal conductivity of three Yb doped samples with a nominal Yb content of 0.2%, 0.5% and 1.0% Yb (I-III) in comparison with the thermal conductivity values reported in the literature [1, 16, 24]. The total thermal conductivity of all three samples is lower than plain Mg_2Si , and is also lower than Bi-doped or Y-doped Mg_2Si ; thus Yb doping provides a more significant reduction in thermal conductivity compared to Y- and Bi-doping. The reduction scales with the amount of Yb, with 1.0% being the lowest; however, the effect at high temperatures is similar for all samples. Since the electronic contributions to thermal conductivity are larger at the higher temperatures, the lack of influence of Yb_3Si_5 precipitates at high temperature is not unexpected. Additionally, since the amount of Yb substitution for Mg is very small, it is the increasing amount of Yb_3Si_5 that scatters long wavelength phonons more effectively, which dominate heat conduction at lower temperature. At the high temperature regime, short-wavelength phonons are mostly responsible for conduction and since phonon-phonon interactions should dominate, the high temperature thermal conductivity is similar for all of the samples. Therefore when adding Bi to the system, only 0.2% Yb was studied (see below). A more detailed image of the thermal conductivity of samples I-III is given in Figure S9 in the Supporting information.

Since Yb^{2+} is isovalent to Mg^{2+} , Yb alloying into the crystal structure of Mg_2Si should only affect the thermal conductivity of the material and have little to no effect on the carrier concentration and mobility. The formation of Yb_3Si_5 inclusions should also lower the thermal conductivity according to Mingos “nano-particle in an alloy” concept [9]. Yb_3Si_5 can be considered a Zintl phase, but shows metallic-like behaviour with mixed-valent Yb [25]. In order to estimate effect of Yb doping on electrical transport in Mg_2Si , the carrier concentration of the solely Yb doped samples with low thermal conductivity (I-III) were determined. The results are listed in Table 2. The determined carrier concentrations are in the same range as the ones of undoped Mg_2Si found in the literature; therefore Yb-doping does not influence the carrier concentrations, as expected.

Figure 3: Comparison of the total thermal conductivity of Mg₂Si from the literature with three Yb-dopant concentrations (0.2%, 0.5% and 1.0%) with literature. The literature values were taken from LaBotz [1] for plain Mg₂Si, Tani [16] for optimally doped Mg₂Si with Bi, and Meng et al. [24] for Y-doped Mg₂Si.

Table 2: Room temperature charge carrier concentrations of plain Mg₂Si and Yb doped Mg₂Si.

ID	Yb (%)	Bi (%)	synthesis	carrier concentration (cm ⁻³)
I	1.0	–	SPS	2.1×10^{17}
II	0.5	–	SPS	7.8×10^{17}
III	0.2	–	SPS	2.9×10^{17}
Lit.[26]	–	–	solid state reaction	3.0×10^{16}
Lit.[26]	–	–	mechanical alloying	2.4×10^{17}
Lit.[27]	–	–	SPS	4.3×10^{17}
Lit.[16]	–	–	vert. Bridgeman growth	8.4×10^{17}

2.3. Optimization of the Microstructure of Bi doped Mg₂Si.

As shown above, the 1% doping of Yb leads to the lowering thermal conductivity, but does not affect carrier concentration. In order to optimize carrier concentration, the sample with 1% Yb and 1% Bi dopants were prepared. The 1% doping with Bi was reported in the literature as an optimized doping concentration [10, 16, 17]. The samples were prepared by the *long ball milling* route (Table 1, Experimental) to ensure the homogenous distribution of Bi dopant.

Figure 4 shows the electrical resistivity of the samples (IV-VII, see Table 1 for details) sintered at various temperatures. (Seebeck coefficient data are provided as Supporting Information, SFigure 11). Samples (1% Yb and 1% Bi) sintered at higher temperatures, 923K and 1023K (V and VI, Table 1), showed lower resistivity, with the lowest resistance for sample VII (1% Bi), prepared by short ball milling.

Figure 4: Temperature dependent behaviour of the electrical resistivity ρ for samples (1% Yb and 1% Bi) IV – black, V – red, VI – blue, (1% Bi) VII – green (See Table 1). The samples

have been ball milled by different approaches and sintered at different temperature showing significant differences in the electrical resistivity.

In order to check for the effect of sintering temperature on microstructure, and consequently, electrical resistivity, scanning electron microscopy (SEM) images of the microstructure of three samples with 1% Yb and 1% Bi (IV-VI) were taken (Fig. 5). The samples were cracked and the fracture faces subsequently etched with methanol (MeOH) in order to enable the SEM microstructure investigations. The grain size of the samples is expected to increase with increasing sintering temperature. Sample (IV) (Fig. 5, *top*) has large grains with sizes up to about 10 μm but they are embedded in a matrix of smaller grains with a pronounced size distribution. With larger magnification it becomes clear that some of the smaller grains (sizes of about 0.5 – 1.5 μm) are also sintered well but again are embedded in a matrix of sub-micron sized particles. In addition, a low degree of small voids are visible which are created during the etching process, as the pellets were fully dense based on geometrical and Archimedes methods. With increasing sintering temperature (samples V and VI) the grain size increases and the amount of sub-micron sized matrix particles surrounding the crystallites decreases (Fig. 5, *middle* and Fig. 5, *bottom*).

Figure 5: SEM images of the MeOH etched fracture faces of 1.0 % Yb doped Mg_2Si sintered at 773 K (sample IV, *top*), 923 K (sample V, *middle*) and 1023 K (sample VI, *bottom*). The precursor material has been prepared by the long ball milling approach. The images show the microstructure of the sample using 5k (*left*) and 20k (*right*) magnification.

The microstructure investigation indicates that all three samples are not well sintered (broad grain size distribution), which can be a reason for the high electrical resistivity. As mentioned before, the samples were prepared by the *long ball milling* method; therefore, severe defects (strain and stress) in the starting material introduced by extended ball milling may negatively impact the microstructure. Additionally, Yb dopant, which was shown to have no effect on carrier concentration, can impact the microstructure by segregating on grain boundaries and impeding the electron transport. Consequently a 1% Bi doped sample (VII) containing no Yb-dopant was prepared by the *short ball milling* approach and sintered at 973 K. Short ball milling can be considered as a mixing rather than a milling process, thus fewer defects are expected. The sintering temperature was chosen, because *Bux* and co-workers state in their work that higher temperatures might lead to significant Mg loss [17]. The electrical resistivity of this sample (VII) is in the expected range for the optimally doped Mg_2Si (Figure 4). The microstructure investigation of sample (VII) (green curve in Figure 4) is shown in Figure 6. A homogeneous grain distribution over the whole sample is apparent. The sample exhibits a well sintered microstructure leading to the lowest electrical resistivity as compared to samples (IV-VI) (Figure 6). The resistivity of the sample (VII), is also in line with resistivities reported in the literature for optimal Bi doping [17].

Figure 6: SEM images of the MeOH etched fracture faces of 1.0% Bi doped Mg_2Si sintered at 973 K (sample VII, *top*) and 1.0% Bi and 0.2% Yb doped Mg_2Si sintered at 973 K (sample VIII, *bottom*). The precursor material has been prepared by the short ball milling approach. The images show the microstructure of the sample using 250 (*left*) and 10k (*right*) magnification.

2.4. Thermoelectric properties of the 0.2% Yb and 1% Bi Mg_2Si sample

Finally, the thermoelectric properties of the sample co-doped with Yb and Bi dopants and their impact on the transport properties are discussed. The lowest Yb concentration of 0.2% was chosen for sample (VIII) in order to avoid the formation of any possible Yb-Bi phases. 1% Bi doping leads to a low electrical resistivity, comparable with other high performance thermoelectric materials. Short ball milling reduces defects in the starting material and sintering temperatures of 973 K are sufficient to obtain fully dense pellets with a well sintered microstructure. Keeping all these factors in mind, sample (VIII) was prepared by spark-plasma sintering as described before (Table 1). The powder XRD of the sample VIII shows that besides the target Mg_2Si phase, the sample contains some MgO and Yb_3Si_5 impurity. The presence of Yb_3Si_5 is not apparent in the 0.2% long ball-milled sample. It is probable that the longer ball-milling times are required for the Yb to replace Mg in the structure and provide a more finely distributed small grains of Yb_3Si_5 , not discernable by powder XRD until 1 at.-%, whereas the short ball-milling time provides large grains of Yb_3Si_5 that can be detected by powder XRD. The short ball-milling time results in larger particle size of Si before the SPS reaction, thus affecting the kinetic of the reaction with YbH_2 and MgH_2 hydrides.

In Figure 7(a) the total and lattice thermal conductivity are shown. The thermal conductivity due to conduction of electrons, κ_e was estimated using Wiedemann-Franz law: $\kappa_e = LT/\rho$, where L is the room temperature Lorenz number, $L = 2.2 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, T -absolute temperature and ρ -electrical resistivity. Consistent with the literature, the lattice thermal conductivity, $\kappa_{\text{lattice}} = \kappa_{\text{total}} - \kappa_e$, has a $\sim T^{-1}$ dependence, which indicates that the phonon-phonon interactions are the primary source of the lattice thermal resistance. Overall, the thermal conductivity of sample co-doped with Yb and Bi is comparable with literature [1, 10, 13, 17]. This is consistent with the interpretation that this sample may not have Yb replacing Mg and large grains of Yb_3Si_5 that do not contribute as efficiently to the phonon-phonon interactions.

Figure 7(b) shows the temperature dependent Seebeck coefficient and the electrical resistivity. The Seebeck coefficient has a negative sign, consistent with an n -type doped material and increases (absolute value) with increasing temperature, which is typical behaviour for a heavily doped semiconductor. The linear temperature dependent trend of the Seebeck coefficient suggests single parabolic band (SPB) behaviour, while the absolute value is comparable with the literature data [17]. The resistivity of the respective sample (Figure 7(b) shown in red) is slightly temperature dependent initially decreasing with temperature followed by a slight increase at $T > 570\text{K}$. Similar temperature dependence of ρ has been reported in nanocomposite samples prepared by reactive sintering of MgH_2 and Si [10]. The

measured carrier concentration amounts to $1 \times 10^{20} \text{ cm}^{-3}$ at room temperature, in range for the optimized carrier concentration for thermoelectric performance of Mg_2Si [10, 17, 18].

Figure 7: Temperature dependence of the (a) thermal conductivity along with the calculated Figure of Merit zT (*inset*) and (b) Seebeck coefficient and electrical resistivity for a 0.2 % Yb and 1.0% Bi co-doped sample of Mg_2Si (Sample VIII, Table 1).

In Figure 7(a) (*inset*) the Figure of Merit zT is shown, calculated from the experimentally determined values. The sample prepared with 0.2% Yb and 1.0% Bi shows a maximum zT of 0.46 at 800 K. The relatively high absolute value of resistivity of $\sim 25 \text{ m}\Omega \text{ cm}$ can be explained by the low carrier mobility, which is most likely caused by ionized impurity scattering or Yb segregation at the grain boundaries. This effect is responsible for the moderate value of thermoelectric figure of merit. By itself, Yb-doping has a positive effect on the thermal transport and does not alter the carrier concentration. However, further optimization is needed as the segregation of Yb at the grain boundaries presumably impedes the electron mobility, thus unfavorably increasing electrical resistivity.

3. Conclusions

Magnesium silicide Mg_2Si is a low density, low cost thermoelectric material which requires tuning in order to achieve suitable Figure of Merit zT values. In our investigations we

focused on samples that were doped with Yb in order to decrease the thermal conductivity. Excess Yb, beyond the potential solubility limit leads to the formation of one of the various Yb_xSi_y phases known in literature [25, 28-33]. With the help of EMPA and STEM structure characterization the Yb dopant is found to be localized in the prepared materials: both the formation of ytterbium silicide Yb_3Si_5 inclusions within the Mg_2Si matrix and segregation of Yb in the grain boundary with Yb substitution of Mg observed. We have investigated the influence of the microstructure on the transport properties of Mg_2Si prepared from MgH_2 and Si in a one-step fabrication process by spark plasma sintering. It is shown that the sintering and ball milling conditions have a significant influence on the microstructure of the final material and consequently on the transport properties. The sample with a co-doping of 0.2% Yb and 1.0% Bi, exhibits a zT of 0.46 at 800 K, which is slightly lower what is reported for the best results from Bi doping in the literature [18]; however, with the understanding gained from the microstructure and the influence of co-doping of the system, further optimization of the Mg_2Si system and additional increases in zT should be possible.

4. Experimental

4.1. Synthesis

Mg_2Si samples doped with Yb were prepared using MgH_2 (Alfa Aesar, powder, 98 %), Si (Aldrich, powder 325 mesh, 99 %), and Yb powder (American Elements, 5N). The Yb powder was determined to be YbH_2 by powder X-ray diffraction and used without further purification. To adjust the carrier concentration, Bi (Johnson Matthey Electronics, rod, 99.9999 %) was added to produce n-type doped materials. All starting materials (total mass of about 12g) were loaded into a tungsten carbide-lined vial with additional O-ring seals in an argon filled glove box. The vial was sealed in a Ziploc bag for an additional oxidation protection for the material during the ball milling process. For the *long ball milling*, all starting materials were added and ball milled for 9 hours in 15 minute on/off intervals using two large tungsten carbide balls. For the short ball milling, Si and Bi were continuously shaken for 30 minutes. The ball mill was transferred into the glove box and MgH_2 and YbH_2 were added, sealed as described above, and the mixture was ball milled for 30 minutes. At the end of the ball milling process, the vial was transferred back into the glove box and stored there. The *long ball milling process* can be considered to be an effective milling step, including particle reduction, while the *short ball milling process* is a mixing rather than milling step. The starting material was reacted and compacted in a one-step reaction using spark-plasma-sintering techniques with the following temperature and pressure profile. The

dopants are provided as at.-%. The SPS experiments were carried out on a Dr. Sinter SPS-825S apparatus (SPS Syntex Inc., Kanagawa, Japan) using graphite dies with a diameter inner diameter 12.7 mm and a sample load of approximately 0.5 g. The temperatures given in Table 1 were measured from the outside of the die with a K-type thermocouple. The dies were aligned in the instrument and dynamic vacuum was applied to the sample chamber. The sample was kept under an axial compressive pressure of 50 MPa. After achieving an acceptable vacuum, the temperature ramped to 623 K within 3 minutes, and then slowly to 723 K within 10 minutes. Since sintering was carried out under dynamic vacuum and the reaction onset was indicated by an increase in pressure caused by the hydrogen released during the reaction. After the reaction ended the pressure was raised to 115 MPa within 2 minutes, while the sample was heated in 10 min to 10 K below the final sintering temperature given in Table 1. The final sintering temperature was reached within 1 minute followed by a dwelling step for 10 minutes before the sample was slowly cooled down to 673 K within 10 minutes. The applied pressure was reduced once the cooling started. An optical image of a pellet obtained by this technique is given in Figure 8.

Figure 8: Optical images of a 12.7 mm pellet of Mg₂Si obtained via spark plasma sintering viewed on a mm grid and photographed at an angle (a) and from on top (b). (c) Bar cut from the pellet for sample VIII which was used for transport property measurements.

4.2. Thermal Analysis

TG/DSC measurements were carried out on a Netzsch STA 409C instrument. Typically 20 mg of the starting material was pressed into a small pellet of 2 mm diameter and transferred into Al₂O₃ crucibles with lid in an argon filled drybox. The samples were transferred into the TG/DSC instrument and heated under a constant Argon stream to 873 K with a heating rate of 10 K min⁻¹. Since H₂ is formed during the reaction, the TG/DSC measurement was only heated till 873 K to protect the platinum parts of the instrument.

4.3. X-ray Powder Diffraction

X-ray powder diffraction data were collected with a Bruker D8 Advance diffractometer using Cu $K\alpha$ radiation (40 KeV, 40 mA) on powders prepared from pulverizing the sintered pellets. Data were collected on a rotating sample (15 rpm) from 10° to 90° (2 Θ), with a step size of 0.01944° and a step time of 1.25 s. Data acquisition was performed using the Bruker Command Center software. Lattice parameter refinements for all present phases as well as full pattern fitting was conducted with the FullProf Suite [34].

4.4. Electron Microprobe Analysis

Fragments of the pressed pellet shaped samples were mounted in epoxy and polished before they were characterized using a Cameca SX-100 electron microprobe equipped with five wavelength dispersive spectrometers. The instrument was operated at 10 kV accelerating voltage and 10 nA current with a beam diameter of approximately 1 μm . Elemental mapping was used to determine the homogeneity of the samples over a region of at least 200 $\times$ 200 μm^2 . Yb, Si and MgO were used as standards for all samples.

4.5. Thermoelectric measurements

Electrical resistivity and Seebeck coefficient were measured on a Linseis LSR3 instrument. The samples were measured in helium atmosphere with ultra-high purity (99.999 %). Thermal diffusivity was measured using a Netzsch laser flash diffusivity system from room temperature to 775 K. The thermal conductivity was calculated using the relation $\kappa = \alpha \cdot C_p \cdot d$, where α is the measured thermal diffusivity, C_p is the specific heat capacity taken from the literature [23] and d is the measured geometric density. The carrier concentration was determined under high vacuum by custom made set-ups described elsewhere [35]. Hall effect of sample VIII was measured by a five-wire measurement on Quantum Design Physical Property Measurement System (PPMS) in the temperature range of 200K -400K and magnetic field up to 5 T. Carrier concentration (n) and electron mobility (μ) were calculated from Hall effect and resistivity (ρ) according to equation: $\rho^{-1} = ne\mu$.

4.6. Scanning Electron Microscopy

Scanning electron microscopy was conducted on a Hitachi S-4100T Hitachi HTA America FE-SEM with an attached Oxford INCA Energy EDS unit.

4.7. Scanning Transmission Electron Microscopy

The electron transparent specimen was prepared by mechanical grinding and polishing using a pellet of Mg_2Si with 1.0% Yb doping. Atomic resolution STEM-HAADF images of the Yb segregation inside the GB were obtained using the Cs-aberration corrected JEOL2100F microscope operated at 200 kV, with a HAADF detector collection angle of 70-190 mrad. The STEM-HAADF images and the EDX spectrum of the Yb_3Si_5 inclusions were acquired using an aberration corrected FEI Titan at 300kV in PNNL.

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