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Towards energy filtering in Mg₂*X*-based composites: Investigating local carrier concentration and band alignment via SEM/EDX and transient Seebeck microprobe analysis

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ABSTRACT

A comprehensive understanding of multi-phase materials requires the characterization of transport properties at the micro/nano-scale. Optimized alignments of the conduction bands and valence bands at the interfaces of multi-phase materials can enhance the properties of thermoelectric materials by filtering out undesired charge carriers and is a promising path towards high performance thermoelectric devices. Here, a micro-scale characterization technique using transient Seebeck microprobe analysis, scanning electron microscopy with energy-dispersive X-ray spectroscopy, and electronic transport modelling based on the Boltzmann transport equation modeling is introduced to assess the band diagram and estimate the band offset in multi-phase materials. This characterization technique is applied to a composite of magnesium silicide-based materials. This material class is prone to form self-assembling nano-structured composites driven by a miscibility gap in the solid solutions series. Our analysis reveals changes in carrier concentration upon composite formation and considerable band offsets for both conduction and valence band when synthesizing nominally undoped composites. Employing Bi as dopant we show that Bi exhibits a preference for the Sn-rich phase, changing the carrier concentration differently in the Sn-rich matrix phase compared to the Si-rich secondary phase, effectively altering the band alignment of the composite. This demonstrates that our approach can be utilized to measure and manipulate the band offset within the composite to achieve optimal thermoelectric performance.

1. Introduction

The necessity to reduce fossil fuel consumption and greenhouse gas emissions has fostered multiple research lines, including conversion of (waste) heat to useful electrical energy through thermoelectric (TE) generators. Application of thermoelectricity relies mainly on two effects: the Seebeck effect and the Peltier effect, which involve the generation of an electric potential when a temperature gradient is applied across a material and the release/absorption of heat at the interface of two materials through which a current is driven, respectively. The efficiency of TE devices depends on the performance of the employed TE materials, which is quantified by the figure of merit (zT) at an absolute temperature T, $zT = (S^2\sigma/\kappa)T$, where S is the Seebeck coefficient, σ represents the electrical conductivity and κ denotes the thermal conductivity. A higher zT value generally signifies higher ability of the material to efficiently convert heat into electricity. Hence maximizing the figure of merit is essential for advancing thermoelectric technologies and enabling applications in waste heat recovery, energy harvesting, and thermal management [1–3].

The TE figure of merit, zT, is inherently limited by the interdependence of the three essential TE transport properties S, σ , κ [4,5]. While optimizing the carrier concentration can improve zT to a certain extent, this limitation can be overcome by employing advanced strategies such as nanostructuring [6–9], isovalent doping for band engineering

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[10–13], phonon engineering [9,14,15], anisotropy design [16–18] and forming nano-composites [19-21]. Modifying electronic band structures through doping is a further promising strategy with several potential benefits, including band degeneracy, band alignment, and the introduction of resonant levels [15,22]. Doping can create resonant impurity levels that interact with band edges, leading to a narrow density of states (DOS) peak near the Fermi level, resulting in higher effective carrier mass and an elevated Seebeck coefficient. Moreover, enhancing band degeneracy through doping, without altering band effective mass, can significantly boost the DOS effective mass, decoupling the Seebeck coefficient from electrical conductivity. Doping can also induce band anisotropy, distorting the spherical electron pocket and promoting transport in the direction of smaller effective mass, ultimately enhancing carrier mobility while preserving a constant DOS effective mass, thereby improving the power factor and zT. Among these strategies, composite materials containing nano-sized precipitates with a tailored electronic band diagram enable the decoupling of TE properties through a process known as energy filtering, where the detrimental spectral fractions of charge carriers are selectively blocked so that they don't contribute to the thermoelectric transport [19,20]. Furthermore, by appropriately sizing the evolving nanostructure, the lattice contribution to the thermal conductivity can be effectively reduced through enhanced phonon scattering at highly concentrated grain boundaries [23,24].

To achieve effective charge carrier filtering in composite materials, a locally varying electronic band structure is essential. In composite materials, the Fermi levels of two phases tend to equalize due to charge transfer, creating barriers caused by shifts in the conduction and valence bands. For an n-type material, optimal energy filtering can be achieved in such multi-phase materials by adjusting a misalignment of the valence band edge to block the conduction of minority carriers and controlling the misalignment of the conduction band edge to balance enhancement of the Seebeck coefficient due to blocking of low energy charge carriers against the reduction of electrical conductivity. This requires dopants for both matrix and secondary phases, ideally selectively doping the target phases to adjust their band positions while also achieving the optimized carrier concentration values required for high performance. Hence, mechanisms to locally adjust or manipulate the band offset are crucial. However, despite numerous reports on reduced lattice thermal conductivity in composite materials [23,25], the successful demonstration of viable thermoelectric materials with decoupled electronic properties and improved power factor through energy filtering strategies remained limited in practical applications [25–27]. Lin et al. recently shed new light on the energy filtering concept by employing a two-phase model [28]. They found that incorporating graphene nanoplatelets into Mg_{3.2}Sb_{1.99}Te_{0.01} increased the Kapitza thermal resistance at the grain boundaries, leading to a heightened temperature drop across the grain boundary region and enhanced interfacial Seebeck coefficient. The challenges faced by previous studies can be attributed to the disconnection between theoretical and experimental approaches. Therefore, to advance this field, a more integrated and comprehensive approach between theory, modelling and experimentation is necessary.

Magnesium silicide-based materials [29–31] (Mg₂X with X = Si, Sn, Ge) are highly promising for energy filtering applications. These materials are cost-effective, and environmentally friendly candidates for thermoelectric generator fabrication, particularly in the mid-temperature range of 500-800 K. These materials exhibit excellent thermoelectric properties, and it is predicted that already single phase Mg₂(Si,Sn,Ge)-based thermoelectric generators could achieve conversion efficiencies greater than 10% [32,33]. On the other hand, the band diagram of a Mg₂X-based solid solutions is expected to vary with changes in the Si to Sn ratio, as the band gap continuously shifts with changing this ratio. Furthermore, there is a reported miscibility gap in this solid solution, with contradictory reports in the literature regarding the compositional boundaries of the miscibility gap of Mg₂Si-Mg₂Sn, suggesting a dependence on processing conditions and magnesium content [34-39]. As a consequence, the solid solutions suffer from phase

separation at high temperatures if uncontrolled magnesium loss occurs, such as through evaporation. However, if this is controlled, the miscibility gap can be advantageous by enabling the formation of in situ nanostructures through stimulated unmixing. Consequently, composites can be formed in two ways in these materials: by mixing different compositions of solid solutions or by self-assembled formation of in-situ nanostructures through unmixing. Selective doping of each phase will then help to optimize the band alignment for effective energy filtering in these materials. Notably, Li and Ag dopants have shown promise for selective doping in p-type Mg₂Sn compared to Mg₂Si [29,40,41]. The doping efficiency of Li was observed to increase with Sn content in Mg₂(Si,Sn), indicating its preferential compositions with higher Sn content. Moreover, experimental evidence supported the preferential doping of Sb in Mg₂(Si,Sn) [42], that aligns with expectations based on different formation energies of dopant-induced defects as indicated by first principle calculations [43].

A comprehensive understanding of multi-phase materials and their integral properties requires the characterization of transport properties at the micro/nano-scale to measure and exploit energy filtering for TE performance optimization. Therefore, the objective of this research is to establish a characterization technique that can accurately quantify the band alignment in both the conduction and valence bands at the interfaces of multi-phase materials, as these alignments are essential for energy filtering. This represents a crucial initial step towards optimizing composite materials through effective energy filtering. The next important step is identifying suitable dopants to precisely adjust the band alignment, thereby further enhancing TE performance. In this study, binary compounds of Mg₂Si and Mg₂Sn were synthesized through mechanical alloying, followed by brief mixing and a combined compaction of the mix to create a composite material. The composite comprises a Sn-rich solid solution matrix with embedded secondary phases, where Si-rich solid solution domains enclose Mg₂Si particles. To estimate the potential barrier at the interfaces, a combination of transient Seebeck microprobe, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), and electronic transport modelling based on the Boltzmann transport equation modeling was employed. The transient Seebeck microprobe enables the measurement of the Seebeck coefficient distribution with µm resolution. This technique is particularly useful for characterizing heterogeneous materials or composite structures where the thermoelectric properties may vary across different phases [44-46]. A compositional map can be obtained by establishing a simple correlation between the grey value in backscattered electron (BSE) images and the chemical composition acquired through calibration by EDX point analysis [47]. Combining the Seebeck coefficient map and the compositional map allows for establishing a local correlation between the Seebeck coefficient and the phase composition in multiphase materials. Moreover, employing two parabolic band (2 PB) modeling with one valence band (VB) and one conduction band (CB) provides insights into the local distribution of the reduced Fermi level and the alignment of valence and conduction bands and allows for the creation of a carrier concentration map. Furthermore, the study demonstrates the potential of selective doping, with Bi identified as a suitable dopant for optimizing band alignment of the different phases. Bi is a popular dopant in various thermoelectric material systems, primarily for optimizing carrier concentration and, to some extent, for engineering the band structure [48,49]. In Mg₂X, its impact on the electronic band structure is relatively limited, but it is employed due to its high dopant efficiency and its favorable effect on reducing lattice thermal conductivity [50–54]. We assumed a rigid band structure with respect to Bi and Mg content, based on existing theoretical and experimental findings and the small variations (<1 at%) for the samples of this study [52,55-58]. This study endeavors to address the existing research gap in composites, where the decoupling of all thermoelectric properties was not yet accomplished.

2. Experimental section

Binary Mg₂Si and Mg₂Sn were synthesized by ball milling of high purity starting elements (>99.5%) using a SPEX 8000D Shaker high energy ball mill. To account for potential Mg loss during synthesis, an excess of 2 at.% of Mg was added, i.e. the nominal compositions were Mg_{2.06}Si and Mg_{2.06}Sn. The binary powders of Mg₂Si and Mg₂Sn were sintered using a direct current sintering press, DSP 510 SE model manufactured by Dr. Fritsch GmbH in Fellbach, Germany. For Mg₂Si, a temperature of 1073 K and a pressure of 66 MPa were applied for a duration of 10 min, while for Mg₂Sn, the temperature was set at 873 K with the same pressure and duration [59]. A composite of (0.5) Mg₂Sn/(0.5)Mg₂Si was prepared by a brief combined milling/mixing of Mg₂Si and Mg₂Sn powder in a 50:50 atomic ratio. Additionally, two other composites of (0.5)Mg₂Sn/(0.5)Mg₂Si_{0.98}Bi_{0.02} and (0.5) $Mg_2Sn_{0.99}Bi_{0.01}/(0.5)Mg_2Si$ were also prepared. The resulting powder samples were then compacted under a vacuum pressure of 10^{-5} bar, applying a pressure of 66 MPa for a duration of 10 min at a temperature of 873 K. The relative densities of the samples were found to be >95% of the theoretical value using Archimedes' method.

The sintered pellets were characterized by performing X-ray diffraction (XRD) using a Bruker D8 with a Co-K_{α} radiation (1.78897 Å). The measurement utilized a step size of 0.01° in the 2 θ range of 20–80°. Backscattered electron (BSE) images were captured using a Zeiss Ultra 55 Secondary Electron Microscope (SEM) equipped with energy Dispersive X-ray (EDX) spectroscopy (PentaFETx3). The compositional map was generated by analyzing the grey values of the pixels in the BSE images with BSE coefficient (η), as described in the methodology discussed in Ref. [47]. This method involved extracting the grey values of each pixel in the BSE images using the software Fiji. η quantifies the relationship between the grey values of BSE images and the chemical composition of the samples. For heavier elements ($Z \ge 10$), η can be expressed as a function of atomic number (Z) using the equation:

$$\eta = \ln \frac{Z}{6} - \frac{1}{4} \tag{1}$$

To calculate the weighted mean BSE coefficient ($\overline{\eta}$) for a compound consisting of *n* elements, the following equation was employed:

$$\overline{\eta} = \sum_{i=0}^{n} C_i \eta_i \tag{2}$$

where C_i represents the weight fraction of element *i*, and η_i represents the BSE coefficient of element *i*. By combining equations (1) and (2) with energy-dispersive X-ray (EDX) point analysis, the BSE coefficient of a compound can be estimated. It has been observed that η exhibits a linear relationship with the grey values. Therefore, if the composition of two points in the BSE images is known, the BSE coefficient of any arbitrary point within the image can be determined using BSE vs. grey value calibration. It should be noted that this calibration is specific to each individual image or each series of images, as long as the settings remain unchanged. The grey value was observed to change with angle of incidence, this can be avoided by using a small area of analysis or high magnification. This method allowed for rapid determination of the local composition (Si to Sn ratio) of a specific sample area with high spatial resolution solely from the EDS analysis of two points.

To obtain a spatial Seebeck coefficient map at room temperature, an in-house developed transient Seebeck microprobe with a spatial resolution of $3-5 \ \mu\text{m}$ was used at DLR [44–46]. It involves placing a fine microprobe on the surface of the material of interest, and then creating a local temperature gradient across the probe. This temperature gradient induces a voltage difference between the two ends of the probe, from which the Seebeck coefficient can be determined. The bulk temperature-dependent Seebeck coefficient and electrical conductivity were measured using a four-probe technique under a helium atmosphere using an in-house developed facility [60,61]. The temperature-dependent

thermal conductivity was determined using the relation: $\kappa = \rho c_p D$, where ρ represents the mass density, c_p denotes the specific heat at constant pressure, and *D* is the thermal diffusivity. The thermal diffusivity (*D*) was measured using a Netzsch LFA 427 apparatus. The specific heat at constant volume (c_v) was estimated using the Dulong-Petil limit, and then c_p was calculated using the equation: $c_p = c_v + 9\alpha^2 T/\beta_T \rho$, where α represents the linear thermal expansion coefficient and β_T is the isothermal compressibility [62–64].

3. Results

BSE images of the composite are presented in Fig. 1a and b. The main contrast in BSE images arises from the differences in atomic number between the constituent materials. It is observed that binary Mg₂Si and Mg₂Sn mixed diffusively and formed solid solutions of varying compositions. SEM and EDX analysis confirmed the presence of Sn-rich matrix phase and Si-rich secondary phase within the composite. The interface between the Si-rich and Sn-rich phases showed a sharp border. Similarly, no continuous transition was observed between black (Mg₂Si) to dark grey phase (Si-rich phase), consistent with the second miscibility gap reported by Yasseri et al. [36]. Alternatively, these sharp domain boundaries can potentially be explained by a significantly higher diffusivity of Sn in Si-rich Mg₂X compared to pure Mg₂Si. The presence of Mg–Sn melt at 600 °C might also have contributed to Sn diffusion in the Mg₂Si phase.

The XRD pattern of the composite displayed peaks corresponding to these phases, as shown in Fig. S1. The XRD pattern reveals broad peaks corresponding to a Sn-rich matrix phase and a Si-rich secondary phase, alongside sharp peak of the Mg₂Si secondary phase. These broad peaks suggest that both the Sn-rich and Si-rich phases do not possess a sharp composition; rather, they exhibit slightly varying compositions. The matrix phase, indicated by a light grey color, exhibited a composition of \sim Mg₂Si_{0.13}Sn_{0.87}. Within the island region, two phases were identified: a dark grey phase, rich in Si with an average composition of \sim Mg₂Si_{0.80}

 $_{\pm 0.05}Sn_{0.20\pm 0.05}$ (as observed from the line scan in Fig. 1c), which enclosed black particles of Mg_2Si.

Fig. 2a-c illustrates the thermoelectric properties of binary Mg₂Si, Mg₂Sn and the composite. Both Mg₂Si and Mg₂Sn demonstrate a negative Seebeck coefficient. The Seebeck coefficient of Mg₂Si initially increases and then decreases with temperature. This sample is moderately doped, exhibiting an electron concentration of approximately 2.0 \times 10^{24} m⁻³ (estimated using 2 PB modeling) at room temperature. At elevated temperatures, the material enters a mixed conduction region, wherein minority charge carriers become activated, leading to a reduction in the Seebeck coefficient value. On the other hand, for Mg₂Sn, the Seebeck coefficient decreases consistently across the measured temperature range, indicating that the sample remains in a mixed conduction state throughout. The electron concentration of Mg₂Sn, estimated using 2 PB modeling, is approximately $2.1 \times 10^{23} \, m^{-3}$ at room temperature. The Seebeck coefficient of the composite is also negative, and it appears to be in a mixed conduction state. In this case, no electronic transport modeling as applies to a single homogeneous phase is applicable as the material is a mixed-phase composite. Furthermore, the electrical conductivity of Mg₂Si first decreases and then increases, in agreement with the trend of the Seebeck coefficient. The electrical conductivity of Mg₂Sn increases with temperature. The difference in electrical conductivity between Mg₂Si and Mg₂Sn is mainly due to their different band gap values, which influence their respective carrier concentrations in particular at high temperature. The Seebeck coefficient and electrical conductivity of the composite follow mostly the classical two-phase composite model, displaying values between those of Mg₂Si and Mg₂Sn phases. At room temperature, the lower electrical conductivity of the composite can be attributed to the expected reduced mobility of charge carriers arising from grain boundary and alloy scattering. The thermal conductivity of Mg₂Si was found to be



Fig. 1. BSE micrographs of the polished surface of the (0.5)Mg₂Si/(0.5)Mg₂Sn composite, with (a) low, (b) high magnification, and (c) EDS line scan.

higher than the reported thermal conductivity values (8–10 Wm⁻¹K⁻¹) [65-67]. For Mg₂Sn, the measured thermal conductivity displayed values 5–7.5 Wm⁻¹K⁻¹, consistent with the values previously reported in the literature [68,69]. The composite showed a lower total thermal conductivity than the binary Mg₂Si and Mg₂Sn, primarily due to the reduced lattice part of thermal conductivity. This reduction is a result of the formation of Si-rich and Sn-rich solid solutions in the composite, leading to Si/Sn alloying and enhanced phonon scattering. The value obtained for the composite in our work is higher than that of the $Mg_2Si_{0.5}Sn_{0.5}$ solid solution [69–72], likely due to the fact that both the matrix phase and the secondary phase on their own have higher thermal conductivities than the Mg2Si0.5Sn0.5 solid solution. Mg2Si and Mg2Sn demonstrated zT values comparable with previously reported data [66, 68,69]. As expected, the figures of merit for all three samples are low as they are undoped, furthermore the figure of merit of the composite is approximately an average of the figure of merit values of Mg₂Si and Mg₂Sn.

Fig. 3a shows a BSE image of the composite, while Fig. 3b represents the corresponding compositional map. In Fig. 3c, the Seebeck coefficient map of the same region is presented. This map illustrates the local variation of the Seebeck coefficient in a multi-phase composite material at room temperature. It was found that in the Sn-rich matrix, the Seebeck coefficient changed to a positive value though it was negative in binary Mg₂Sn (Fig. 2a). This transition suggests a change of the dominant charge carrier type, potentially influenced by alterations of point defect types, charges and concentrations. Among the known native point defects in Mg_2Si and Mg_2Sn , it is established that Mg vacancies act as an acceptor [73,74]. Consequently, the positive Seebeck coefficient observed in the Sn-rich matrix may be attributed to a deficiency in magnesium, resulting from the diffusion of Mg atoms from the Sn-rich region to the Si-rich region.

The carrier concentration map can be derived from the Seebeck coefficient map using electronic transport modeling, provided the effective mass of the region is known. In the composite, we observe regions of small negative and positive values of the Seebeck coefficient, possibly indicating mixed conduction behavior. In such cases, consideration of electrons and holes in a two-parabolic band (2 PB) model is necessary.

The charge neutrality equation is employed, wherein the net extrinsic carrier concentration (N_{extr}), is represented as the difference between the concentrations of the two types of carriers [75]:

$$N_{\rm extr} = n_{\rm maj} - n_{\rm min} \tag{3}$$

For a system with two parabolic bands, the properties are described by the following equations:

$$S = \frac{S_{CB}\sigma_{CB} + S_{VB}\sigma_{VB}}{\sigma_{CB} + \sigma_{VB}}$$
(4)

$$\sigma = \sigma_{CB} + \sigma_{VB} \tag{5}$$

where *S* is the Seebeck coefficients and σ is the electrical conductivity.



Fig. 2. Temperature dependence of (a) Seebeck coefficient, (b) electrical conductivity, (c) total thermal conductivity, and (d) figure of merit of binary Mg₂Si, Mg₂Sn and the (0.5)Mg₂Si/(0.5)Mg₂Sn composite.

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The Seebeck coefficient of each band (S_i) , is given by the equation:

$$S_i = \frac{k_{\rm B}}{e} \left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right) \tag{6}$$

Here, *e* is the electronic charge, η the reduced Fermi level with respect to the considered band, F_j is the Fermi integral: $F_j(\eta) = \int_0^\infty \frac{e^j d\varepsilon}{1 + \exp(\varepsilon - \eta)}$, and ε is the reduced energy.

It is essential to emphasize that the position of the reduced Fermi level is considered relative to the band edge associated with the transport property being calculated. When the conduction band edge is selected as the reference, the reduced Fermi level with respect to the valence band is expressed as $\eta = -\psi - \varepsilon_{\rm g}$. Here, ψ represent the reduced Fermi level of the valence and conduction bands, and $\varepsilon_{\rm g}$ denotes the reduced band gap $\left(= \frac{E_{\rm g}}{k_{\rm B}T} \right)$, where $k_{\rm B}$ is Boltzmann's constant.

The carrier concentration of each band (n_i) is related to the density of states effective mass $(m_{D,i}^*)$ and the reduced Fermi level η through the equation:

$$n_i = 4\pi \left(\frac{2m_{\rm b}^* k_{\rm B} T}{h^2}\right)^{\frac{3}{2}} F_{\frac{1}{2}}(\eta) \tag{7}$$

The conductivity is related to mobility parameter, μ_0 by [76]:

$$\sigma_i = n_i e \mu_0 \frac{2}{3} \frac{F_0}{F_{1/2}}$$
(8)

The mobility parameter caused by acoustic phonon scattering is expressed by:

$$\mu_{0,\text{AP}} = \frac{\pi \sqrt{8}\hbar^4 e\rho v_l^2}{4E_{1ad}^2 m_s^{2.5} (k_B T)^{\frac{3}{2}}}$$
(9)

Here, ρ represents the material density, v_l denotes the longitudinal sound velocity, $m_{\rm s} = m_{\rm D}^*/N_{\rm v}^{2/3}$ is the single valley effective mass, used to calculate carrier mobility and electrical conductivity, \hbar is the reduced Planck's constant and $E_{\rm def}$ is the deformation potential constant. $N_{\rm v}$ is the valley degeneracy.

The mobility parameter due to alloy scattering is given by [77]:

$$u_{0,\text{AS}} = \frac{64e\hbar^4 N_0}{9(2\pi)^{\frac{32}{2}} x(1-x) E_{\text{AS}}^2 m_s^{2.5} (k_{\text{B}}T)^{\frac{12}{2}}}$$
(10)

where N_0 is the number of atoms per unit volume, *x* represents the Sn fraction at the *X* position in Mg₂(Si,Sn) and E_{AS} is the alloy scattering parameter.

When both alloy scattering and acoustic phonon scattering are present, the mobility is determined by Matthiessen's rule [41,78]:

$$\frac{1}{\mu_0} = \frac{1}{\mu_{0,AP}} + \frac{1}{\mu_{0,AS}}$$
(11)

The parameters used for 2 PB calculations are listed in Table 1.

By using the above equations, the carrier concentration can be estimated from the Seebeck coefficient values. However, to perform these calculations, knowledge of the effective mass is necessary. In the case of composites comprising both p-type and n-type materials, it is essential to develop a model for the density of states (DOS) effective mass that considers the conduction band (CB) and valence band (VB) masses as a function of composition. To obtain an effective mass map for the n-type



Fig. 3. (a) The backscattered electron (BSE) image, (b) its corresponding chemical compositional map, (c) Seebeck coefficient map measured by the transient Seebeck microprobe (TSM), and (d) carrier concentration map of the $(0.5)Mg_2Si/(0.5)Mg_2Sn$ composite.

 Table 1

 Material parameters used for 2 PB transport calculations of Mg₂Si_{1-x}Sn_x.

Parameter	Value
$E_{\rm g}$ (eV)	$(0.78 - 4.0 \times 10^{-4} \times T) \times (1 - x) + (0.28 - 2.0 \times 10^{-4} \times T) \times x$ [75.79]
E _{def} for conduction band (eV)	$9.0 - 1.5x^2$ [79]
E _{def} for valence band (eV)	9 [41]
$E_{\rm AS (eV)}$	0.5 [41]
$v_l (m/s)$	7680 - 2880 x [41]
ρ (kg/m ³)	1990(1-x)+ 3590 x [79]
N_V for VB	2 [75]
N_V for CB	3 [75]
$N_0 \ ({ m m}^{-3})$	$12 imes 10^{30}/(6.37+0.45~{ extsf{x}})^3$

ternaries, an interpolation method was employed using existing experimental data from literature [42,80–82] (Table S1). These previous reports also assumed acoustic phonon scattering and alloy scattering as the predominant scattering mechanisms, aligning with the model employed in our study.

For the p-type $Mg_2Si_{1-x}Sn_x$, the effective mass map as a function of composition was derived using the approximate equation:

$$m_{D,P}^* = (2.2 - 1.1x)m_0 \tag{13}$$

This linear relation is backed up by experimental data for Sn-rich compositions [41] and by the predictions from first principles calculations [83]. Consequently, through the consideration of respective compositions, two distinct effective mass maps were obtained: one for the n-type composition and another for the p-type composition. These maps were then utilized to generate the carrier concentration map, considering the effective mass based on the composition. Figs. S2a and S2b represent effective mass maps for electrons and holes, respectively.

Fig. 3d presents the carrier concentration map of the composite material which was obtained using the 2 PB model. Two possible carrier concentration values were derived for each Seebeck coefficient, and the lower values (corresponding to mixed conduction) were selected to create the effective mass map (Fig. S3 and Fig. S4). The carrier concentration map reveals that the Si-rich region exhibits a p-type carrier concentration, despite having a negative Seebeck coefficient value, while the Sn-rich region exhibits an n-type carrier concentration and a positive Seebeck coefficient value. To provide a clearer visualization, a line scan along y = 0.5 of the map for the Si content, Seebeck coefficient, and carrier concentration are plotted in Fig. 4. In the plot, the bluecolored region represents the Si-rich phase, while the red-colored region represents the Sn-rich phase. Within the blue-colored region, the Si content is close to 1, and the Seebeck coefficient ranges from -200 to -250 μ V/K. Remarkably, even though the majority charge carriers are holes (p > n), the Seebeck coefficient remains negative. This behavior can be attributed to the higher mobility of electrons in Mg₂Si, which is approximately ten times higher than that of holes, a factor we



Fig. 4. (a) Si content, (b) Seebeck coefficient, and (c) carrier concentration profiles along a line scan at y = 0.5 of the maps shown in Fig. 3c and d.

considered in our 2 PB modeling [30,84]. Therefore, although the number of holes is higher, the contribution from the electrons dominates in the Seebeck coefficient. Conversely, in the red-colored region, the Si content is around 0.2, and the Seebeck coefficient displays a small positive value. Interestingly, the electron concentration now surpasses the hole concentration (n > p). This phenomenon arises as a result of considering the higher hole mobility of Mg₂Sn compared to electrons in the 2 PB calculation [41].

The band structure diagram of the composite material, consisting of a Sn-rich matrix and Si-rich secondary phases, is displayed in Fig. 5. In this analysis, a typical equilibrium scenario over the main miscibility gap of the Mg₂X solid solution series is considered but binary Mg₂Si that was also found in the microstructure of our samples is omitted. The reduced Fermi level of the matrix phase and secondary phases was estimated from the



Fig. 5. A schematic representation of the band diagram of the composite containing the Sn-rich matrix and the Si-rich secondary phase. The reduced Fermi level was estimated from the Seebeck coefficient values using 2 PB transport modeling.

averaged Seebeck coefficient values over space (Fig. 3c) using 2 PB transport modeling. This provided the relative positions of the Fermi level with respect to the conduction band minima for the matrix ($E_{\rm F} - E_{\rm c} = -0.14 \, {\rm eV}$) and secondary phase ($E_{\rm F} - E_{\rm c} = -0.30 \, {\rm eV}$), respectively. For the specific composition Mg₂Si_{0.13}Sn_{0.87}, the band gap of the matrix phase (denoted by subscript "m") was estimated to be ($E_{\rm c,m} - E_{\rm v,m}$) = 0.29 eV (Table 1) (at room temperature). Similarly, the band positions were estimated for the Si-rich secondary phase. For the composition Mg₂Si_{0.85}Sn_{0.15}, the band gap of the secondary phase (denoted by subscript "s") was found to be ($E_{\rm c,s} - E_{\rm v,s}$) = 0.59 eV. The potential barrier height at the conduction band, as depicted in Fig. 5, can be calculated as follows: $E_{\rm barrier,CB} := (E_{\rm c,s} - E_{\rm c,m}) = (E_{\rm c,s} - E_{\rm F}) - (E_{\rm c,m} - E_{\rm F}) = 0.16 \, {\rm eV}$ and at the valence band: $E_{\rm barrier,VB} := (E_{\rm v,m} - E_{\rm v,s}) = (E_{\rm c,s} - E_{\rm v,s}) - (E_{\rm c,s} - E_{\rm v,s}) - (E_{\rm c,m} - E_{\rm v,s}) - (E_{\rm c,m} - E_{\rm v,m}) = 0.14 \, {\rm eV}$.

The situation shown in Fig. 5 is not optimized for thermoelectric performance: the overall carrier concentration is too low and a handle to modify the band positions of the matrix phase with respect to the secondary phase is missing. For this reason, doping using Bi was investigated, as Bi has been proven as an efficient and stable n-type dopant for magnesium-silicide based materials [50,51,54,81,85]. Therefore, in this study, we prepared two composites, (0.5)Mg₂Sn_(0.5)Mg₂Si_{0.98}Bi_{0.02} and (0.5)Mg₂Sn_{0.99}Bi_{0.01}/(0.5)Mg₂Si to investigate the effect and a potential preference of Bi to the Si-rich phase or Sn-rich phase.

Fig. 6a displays the BSE images of the (0.5)Mg₂Sn/(0.5) Mg₂Si_{0.98}Bi_{0.02} composite, while Fig. 6b shows the elemental map of Bi from the same region. The composite structure consists of a Sn-rich matrix phase along with a Si-rich secondary phase exhibiting varying Si-content and an encapsulated Mg₂Si phase. At the core of the island phase, a cloud-like structure emerges as a result of the higher Si content at the center and lower Sn content. The Bi content is highest in the matrix phase, which is uniformly distributed throughout the matrix and lowest in the Mg₂Si islands within the Si-rich phase, revealing Bi redistribution during composite sintering. The small visible increase in Bi content towards the center of the large Si-rich island can be interpreted as result of Bi diffusion into the Sn-rich matrix. Fig. S5 depicts the BSE image and elemental map of Bi acquired from the (0.5) $Mg_2Sn_{0.99}Bi_{0.01}/(0.5)Mg_2Si$ composite. Also, in this case, the elemental map clearly reveals that the Si-rich island phase contains a lower Bi concentration compared to the Sn-rich matrix. To support this observation, EDX point analysis was conducted for each phase in these two composites, and the results are provided in the supplementary information (Tables S2 and S3). Combining the elemental mapping data with the EDX point analysis, it can be concluded that Bi has a clear preference





Fig. 6. (a) BSE image and (b) corresponding elemental mapping image of Bi obtained through EDX mapping of a $(0.5)Mg_2Sn/(0.5)Mg_2Si_{0.98}Bi_{0.02}$ composite.

for Sn-rich compositions. The amount of Bi systematically decreases with decreasing Sn content, and no Bi is detected in the Mg₂Si phase. Consequently, the Si-rich secondary phase, which contains a significantly lower amount of Sn, exhibits a minimal presence of Bi.

Fig. 7 displays the BSE image and corresponding Seebeck coefficient map of $(0.5)Mg_2Sn/(0.5)Mg_2Si_{0.98}Bi_{0.02}$ composite. The Seebeck



Fig. 8. A schematic representation of the band structure of $(0.5)Mg_2Sn/(0.5)$ $Mg_2Si_{0.98}Bi_{0.02}$ composite containing both the Sn-rich matrix and the Si-rich secondary phase.

coefficient map and BSE image clearly reveal two distinct regions: the Sn-rich matrix and the Si-rich secondary phase, each having different Seebeck coefficient values. In this case, the Seebeck coefficient of the Sn-rich matrix was observed to be negative and $-150 \,\mu$ V/K. This is a typical value for a highly doped sample and in agreement with Bi known to be a good n-type dopant. The average Seebeck coefficient values obtained from the plateau region of each domain ($-75 \,\mu$ V/K for Si-rich secondary phase and $-150 \,\mu$ V/K for Sn-rich matrix) were used to estimate the potential barrier at the interface of this composite.

The schematic in Fig. 8 illustrates the band structure of the (0.5)Mg₂Sn/(0.5)Mg₂Si_{0.98}Bi_{0.02} composite. The introduction of Bi dopant significantly altered the position of the Fermi level in the Sn-rich matrix. It also changed the Fermi level position of the Si-rich secondary phase slightly, possibly because a small amount of Bi was present in the Si-rich secondary phase. Considering that the matrix was doped with Bi, the higher carrier concentration/reduced Fermi level corresponding to the measured Seebeck coefficient was employed for the matrix phase, corresponding to electron-dominated transport. This assumption was motivated by the observed increase in the Seebeck coefficient of Bidoped Mg₂Sn with temperature, which strongly indicates its doped nature (Figs. S6 and S7). The reduced Fermi level of the Sn-rich matrix was found to be $(E_f - E_c = 0.03 \text{ eV})$, and for the Si-rich secondary phase, it was $(E_f - E_c = -0.27 \text{ eV})$. As a result, barrier heights of 0.30 eV at the conduction band was obtained. This change in reduced Fermi level indicates that selective doping of each phase can change the height of the potential barrier.



Fig. 7. (a) The backscattered electron (BSE) image, and (b) Seebeck coefficient map measured by the transient Seebeck microprobe (TSM) of the $(0.5)Mg_2Sn/(0.5)$ $Mg_2Si_{0.98}Bi_{0.02}$ composite.

4. Discussion

X-ray (Fig. S1) and SEM investigation (Fig. 1) showed that in the composite made from Mg₂Si and Mg₂Sn involving some high temperature steps, the two components do not persist in their binary composition but instead, driven by solid state diffusion, form solid solutions with varying compositions. Within the composite, a Sn-rich solid solution was identified as the matrix phase, enclosing domains of a Si-rich solid solution that contains inclusions of pure Mg₂Si as a residual phase. This observation can be attributed to the relative softness of Mg₂Sn compared to Mg₂Si, which can be attributed to the atomic size and bonding characteristics of Sn and Si with Mg. Due to its larger atomic size, Sn exhibits weaker atomic bonding, resulting in lower hardness and contributing to a softer material. Additionally, the band gap of Mg₂Sn is smaller, resulting in weaker bonding overall. Previous studies [86-88] have also demonstrated that Mg₂Sn exhibits a higher degree of softening at elevated temperatures compared to the samples containing Si (including solid solutions and binary Mg₂Si). Conversely, Mg₂Si possesses a relatively high Young's modulus and stiffness due to the strong covalent bonds between silicon and magnesium atoms. During the sintering process at 873 K, when phase formation occurs, the softer nature of Sn-rich solid solution allows it to fill the gaps, while Si-rich composition behaves as the residual phase, likely due to its higher stiffness and more stable bonding characteristics.

There was no binary Mg₂Sn left in the composite after the high temperature compaction step. However, smaller grains of the binary Mg₂Si compound were observed, surrounded by the Si-rich solid solution. This phenomenon can be attributed to the diffusion of Sn (the largest atom) in Mg₂Si (with the smallest lattice constant), which appears to be impeded, leading to the prolonged presence of Mg₂Si particles which rather slowly dissolve from the surface. The sharp domain interface of the Mg₂Si grains clearly indicate incomplete solubility of Mg₂Si/Mg₂Sn for certain compositions so that only when a certain level of Sn concentration is reached near the Mg₂Si grain surface, Si and Sn interdiffusion can occur. Due to the short sintering time of 10 min, complete diffusion of Si and Sn did not occur, and the system did not reach equilibrium. The interdiffusion between Si and Sn can also be influenced by the surrounding Mg content and diffusion of Mg. The grain boundaries also have a significant influence on the diffusion process. The morphology observed in the micrographs (Fig. 1) clearly indicates that the migration of Sn into Si-rich domains tends to occur preferentially along grain boundaries, while the reverse is also evident, where Si migrates into Sn-rich domains.

The compositions of each phase in the composite material are controlled by the limited solubility of Si in Mg₂Sn and Sn in Mg₂Si. Even though the composites are not in thermodynamic equilibrium the relatively large and homogeneous regions make a comparison with previous reports reasonable. We find that the Sn-rich Mg2Si0.13Sn0.87 fits relatively well to the thermodynamic prediction from Viennois et al. [37], while the Si-rich Mg₂Si_{0.80±0.05}Sn_{0.20±0.05} is in very good agreement with the experimental results from Yasseri et al. [36] who found a miscibility gap for 0.35 < x < 0.95 at T = 600 °C within which an extended region with miscibility for 0.75 < x < 0.85 was found; thus the Si-rich phase observed here fits very well with the left ear of the "miscibility cat". The limits of the miscibility gap are disputed, but it was argued that coherency of the grain interfaces plays an important role, partially explaining conflicting results [34,35,89]. We clearly find here that mixing of binary Mg₂Si and Mg₂Sn leads to the formation of a composite with predetermined compositions for each phase, in accordance with the miscibility gap.

The Seebeck coefficient map of the composite without external dopant in Fig. 3c indicates Mg diffusion from Sn-rich matrix to Si-rich matrix. In the binary Mg₂Sn phase, the calculated carrier concentration was 2×10^{23} m⁻³, with a Seebeck coefficient of approximately – 250μ V/K. However, in the composite, the Seebeck coefficient of the Sn-rich matrix changed to a positive value despite the majority of charge

carriers remaining as electrons. The transition from a negative to a positive Seebeck coefficient suggests a decrease in electron concentration, potentially due to Mg vacancy formation. As depicted in Fig. 4, the absence of any gradual transition in carrier concentration within both the Si-rich and Sn-rich regions indicates that Mg diffusion reached equilibrium, even within the short sintering time. Consequently, we can infer that Mg diffusion occurs at a faster rate compared to Si and Sn diffusion. This is in accordance with previous studies which showed that Mg appears to interact more rapidly with the surrounding atmosphere, influencing its concentration within the material [62,90,91]. We note that we find indications for Mg re-distribution on a µm scale, but that this is not caused by (selective) Mg loss as the same is macro-homogeneous with respect to the carrier concentration as visible from the large-scale scan shown in Fig. S8. Typically, defect densities increase when transiting from Mg₂Si to Mg₂Sn [73]. We can qualitatively conclude from the observed change to p-type for the Sn-rich matrix that vacancy formation is favored in Sn-rich compared to Si-rich, in agreement with point defect formation energy calculations for the binaries [73,74].

Fig. 5 provides a visual representation of the band structure of the matrix and secondary phases when they are connected in the composite phase. Understanding and quantifying this potential barrier is crucial for optimizing the thermoelectric performance of the composite material. Bahk et al. [79] conducted theoretical estimations by considering a parabolic band model and an energy-dependent electron scattering time and proposed an optimized potential barrier of 0.4 eV at the conduction band. Their calculations showed that such optimization could elevate the figure of merit from 1.2 (for the bulk material) to 3 (for the composite) at a temperature of 700 K, with a doping density of 1×10^{27} m⁻³. It is also important to experimentally quantify the potential barrier to establish an optimized scenario for magnesium-silicide-based materials. This understanding will facilitate the exploration of different dopants to adjust the band positions, thereby tuning the potential barrier and doping density values in this material. By effectively manipulating these parameters, the thermoelectric properties of the material can be further enhanced.

Kosonowski et al. [92] conducted a similar analysis to quantify the potential barrier in a CoSb3-PbTe composite. In their study, they estimated the reduced Fermi level positions of each phase by separately measuring the Seebeck coefficient of bulk CoSb₃ and PbTe materials. However, it is important to note that the behavior of these phases can differ when they are in the composite form due to element redistribution or reactions between them. Microstructural analysis can provide some insights into the phase composition of each component in the composite. However, subtle changes in composition may not be easily detectable in micrographs, despite their significant impact on the Seebeck coefficient and overall thermoelectric performance. For instance, in our investigations of the Mg₂Si-Mg₂Sn composite, we observed changes in phase composition through microstructural analysis. However, the deficiency of magnesium could not be identified through this method. Instead, it was successfully detected by mapping the Seebeck coefficient using a transient Seebeck microprobe. Therefore, to accurately estimate the potential barrier at the interfaces, obtaining a local map of the Seebeck coefficient within the composite is necessary. On one hand, our microstructure of the composite is not fine enough to cause the desired functional effects of energy filtering with a large impact in integral level. On the other hand, a suitably fine nanostructure would not allow us to resolve Seebeck values locally. Hence, our micro-grained composites serve as a necessary pre-stage in our methodology for the development of optimized target systems. This approach provides a more comprehensive understanding of the thermoelectric behavior and allows for the characterization of subtle variations in composition that might not be apparent through traditional microstructural analysis.

In this work, the preference of Bi dopant and its effect on the band offset in the target composite has been investigated. Through the elemental mapping in Fig. 6 and Fig. S5, along with EDX point analysis

(Tables S2 and S3), it was observed that Bi predominantly resides in the Sn-rich phase. The Seebeck coefficient of the Sn-rich matrix was observed to be negative. The presence of Bi was also evident in the Sirich secondary phase, as indicated by the Seebeck coefficient map. In the Si-rich secondary phase, the Seebeck coefficient was measured to be around $-75 \,\mu\text{V/K}$ (Fig. 7), whereas it was approximately $-250 \,\mu\text{V/K}$ in the case of the non-doped sample (Fig. 3). Comparing the barrier heights in Figs. 5 and 8 shows that Bi can be used to adjust the Fermi levels in the two phases differently, enabling tuning of the barrier height between the phases of the composite. Bi also effectively serves as a dopant for both the binaries and as well as the composite materials (see Fig. S6 and Fig. S7 for the temperature dependent bulk properties of the doped composites). This observation is in line with the discussed band structure, where a significant shift of the Fermi level toward the conduction band was evident. Interplay of doping by Bi with self-doping by Mg or use of a further dopant with different preference between Si-rich and Snrich solid solutions can then allow to tune the barrier height for optimized energy filtering and thermoelectric properties of the material.

In order to obtain the band schematics, the reduced Fermi energy was calculated using 2 PB modeling. While the obtained carrier concentration values are model-dependent and may not always be perfectly accurate, they do offer valuable qualitative insights into the change in carrier concentration with composition, aiding in our understanding of Mg diffusion in the material. Future work should involve consideration of a further conduction band for the description of Mg₂X, as this is known to influence the transport for some compositions, especially those around Mg₂Si_{0.3}Sn_{0.7} [30,82].

Our method involves characterizing the material at the micro-scale using transient Seebeck microprobe analysis. However, in suitable composites for efficient energy filtering, the size of the intermittent phase domains falls within the lower nanometer range, preventing to resolve plateau values of the Seebeck coefficient over single domains by the transient Seebeck microprobe. To address this limitation, nano-scale characterization techniques are required. One such technique is Kelvin Probe Force Microscopy (KPFM) [92–96], which offers a spatial resolution of around 20 nm and can provide the value of the Fermi level position with respect to the vacuum level. By combining KPFM with SEM/EDS and first principle calculations, we may effectively resolve the local band structure variation and properties of materials at the nano-scale.

5. Conclusions

In conclusion, this study aimed to explore methodologies to estimate the potential barriers at the conduction and valence bands and to locally resolve the carrier concentration in a magnesium silicide-based microcomposite. The composite, synthesized by mixing binary Mg₂Si and Mg₂Sn pre-milled powders, exhibited the formation of solid solutions with varying compositions, facilitated by solid-state diffusion. The composite exhibited a Sn-rich solid solution as the matrix phase, enclosing domains of a Si-rich solid solution with inclusions of pure Mg₂Si as a residual phase. Utilizing the transient Seebeck microprobe, we obtained a Seebeck coefficient map that provided valuable insights into Mg diffusion from the Sn-rich phase to the Si-rich phase. Using this data, a carrier concentration map was generated by incorporating effective mass values from literature. Transport modeling, employing a two-band model, allowed us to determine the reduced Fermi level, which facilitated the estimation of the band alignment at the interface of the composite. Furthermore, the study aimed to adjust the band offset through selective doping. Our findings prove that Bi has an affinity to the Sn-rich phase and can be effectively utilized to fine-tune the band positions of the Sn-rich matrix phase. This confirms the possibility of adjusting the band offset through the interplay of Bi doping or the use of other dopants. Local characterization of these multi-phase materials and precise manipulation of the band offset at the micro scale are crucial initial stages in the optimization process of composites, facilitating effective energy filtering strategies.

Credit author statement

Sanyukta Ghosh: Conceptualization, Data curation, Validation, Analysis, Writing original draft. Harshita Naithani: Modeling transport properties, Discussions, Writing: Reviewing and Editing. Byungki Ryu: Discussions and Suggestions on the study, Writing: Reviewing and Editing. Gregor Oppitz: Handling transient Seebeck microprobe, Discussions and suggestions. Eckhard Mueller: Supervision, Writing: Reviewing and Editing. Johannes de Boor: Conceptualization, Methodology, Validation, Supervision, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtphys.2023.101244.

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