High-Performance Thermoelectric Devices Made Faster: Interface Design from First Principles Calculations

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The enormous progress achieved with high-performance thermoelectric materials has yet to be implemented in high-performance devices. The bottleneck for this is the material-specific design of the interface between the thermoelectric material and the electrical connections, particularly identifying suitable contacting electrodes. This has mainly been empirical, slowing down device maturation due to the vast experimental space. To overcome this, an electrode pre-selection method based on first-principles electronic structure calculations of charged defect formation energies is established in this work for the first time. Such method allows to predict thermoelectric leg degradation due to impurity diffusion from the electrode into the thermoelectric material and formation of charge carrier traps, causing a majority carrier compensation and performance deterioration. To demonstrate the feasibility of this approach, the charged point defect formation energies of relevant metal electrodes with Mg₂(Si,Sn) are calculated. Five hundred ten defect configurations are investigated, and the interplay between intentional doping and electrode-induced point defects is predicted. These predictions are compared with Seebeck microprobe measurements of local carrier concentrations near the Mg₂(Si,Sn)-electrode interface and a good match is obtained. This confirms the feasibility of electrode screening based on defect formation energy calculations, which narrows down the number of potential electrodes and accelerates device development.

are an integral part of different industries and find applications in PCR cyclers, cooling of electronic devices, and thermal management in electrical vehicles. Thermoelectric generators (TEGs), on the other hand, are used in several industries for power generation by converting waste heat into electricity. As they are compact, loss-less scalable, and virtually maintenance-free, they also hold great potential for powering autonomous sensors, providing the backbone for the IoT.^[1] The performance of TE devices (power output, cooling power, and conversion efficiency) is governed by the thermoelectric properties of the employed TE materials as well as the electrical and thermal losses through resistances at the multiple material interfaces in the device.^[2] Building a functional TE device thus necessitates both efficient n- and p- type thermoelectric materials, as well as optimized contacts using metallic electrodes to efficiently connect the single legs of the TEG. Designing these interfaces is therefore as critical as optimizing the TE material, and failing to do so leads to reduced

1. Introduction

Thermoelectric (TE) devices are employed as heat pumps for temperature regulation based on the Peltier effect or for conversion of heat into electricity based on the Seebeck effect. TE heat pumps

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device performance and even device failure.^[3] Therefore, thermoelectric research is increasingly focusing on the contacting procedure to translate the impressive progress in material design into efficient device development. However, with a few recent exceptions,^[4] contact development has been mainly

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One challenge in contact development is the possible degradation of the TE material due to (charged) point defects induced by the electrode causing a change of the carrier concentration.^[6] The performance of a TE material is determined by its dimensionless figure of merit $zT = \frac{S^2\sigma}{T}$, where *S* is the Seebeck coefficient, σ is the electrical conductivity, κ is the total thermal conductivity and T is the absolute temperature. Each of the three material properties is sensitive to the charge carrier concentration,^[7] and therefore a delicate balance has to be found for optimized performance. Beyond the direct impact of reduced material performance, an unintended change in carrier concentration has a further detrimental effect on the device level: the cross-section ratio of n- and p-type legs is typically adjusted to allow for an optimized current density in both legs simultaneously,^[8] In fact, a property change in one leg type will deteriorate device performance because geometric compatibility is not given any more. An electrode-induced change in carrier concentration will therefore lead to TE devices with potentially massively inferior performance.

Electrode-induced material property change was recently observed in a contacting study using Ag as electrode for Mg₂X.^[6a] The study also found that the Ag-induced reduction in carrier concentration leads to a reduction of the figure of merit by almost 50%, highlighting the potential impact of the effect. Reassessing existing reports, it is easily found that this is a general phenomenon that is neither specific to Ag as electrode material nor Mg_2X as TE material. In fact, the possibility of charge carrier concentration changes close to the interface when Ag is employed as electrode material for PbTe was discussed in previous work, and material degradation was observed with Cu and $Ni_{45}Cu_{55}$ electrodes when contacted with Mg₂X; similarly, a local reduction in carrier concentration was found for a PbTe/Fe-Sb interface. $^{[4c,6b,c,9]}$ Interestingly, this degradation was observed only for one type of majority carriers of the TE materials: a change in the TE properties after contacting with Ag, for example, was only recorded for the n-type Mg₂(Si,Sn) material while no degradation was observed for the p-type counterpart. Further research showed that this charge compensation mechanism is not strongly related to neither the newly grown reaction layer between the TE material and the electrodes nor the electrical sintering current that the samples are subjected to during the contacting procedure in the direct sinter press.^[6b,c,10] Instead, it has been argued that the observed material degradation is majorly due to defect diffusion from the electrode to the TE material. Given the ubiquity of point defects and their crucial role in TE (and other) functional materials one might wonder why this problem has not appeared more prominently beforehand.^[11] TEGs are usually characterized by integral measurements, particularly (open circuit) voltages and bulk resistances. The formation of electrode-induced point defects causes a change in both, but so would other change mechanisms like material degradation

due to thermal load or crack formation.^[8a,12] A typical fingerprint for electrode-induced point defects is gradients in the TE properties, at least in the initial stage of diffusion. These are not easily recognized by integral measurements but are identified by microprobe measurements. Comparing the typically available Seebeck coefficient and electrical potential measurements, we note that a change in carrier concentration directly affects the locally measured Seebeck coefficient but modifies only the slope of the electrical potential. Seebeck microprobe measurement are therefore the most suitable tool to detect changes in carrier concentration, even if potential measurements can also be employed to that purpose. $^{[4c,1\bar{2}]}$ As on the one hand the fabrication of TE devices usually involves high-temperature steps which would facilitate electrode-induced defect formation but on the other hand (postmortem) microprobe characterization is not common, we speculate that electrode-induced material degradation is common but often goes unnoticed.

Electrodes causing a change in carrier concentration must therefore be avoided for device fabrication. Experimentally testing the TE materials of interest with different electrodes to establish if material degradation occurs or not is very costly and timeconsuming. Consequently, a fast and reliable pre-experimental theoretical method is desirable to predict the potential effect of electrode-induced defects on the TE material. In a previous work of Ayachi et al., such hybrid-DFT calculations were utilized to study the influence of the Ag-induced defects on Bi- and Li-doped Mg₂Si and Mg₂Sn.^[6a] The study showed a good match between the observed experimental findings and the consequences deduced from the hybrid-DFT calculations, establishing that the proposed calculation method could successfully predict material degradation in n-type Mg₂Si and Mg₂Sn and no material degradation in p-type Mg₂Si and Mg₂Sn.^[13] This indicates that Hybrid-DFT calculations of defect formation energies have the potential to predict electrode-induced degradation of the TE material. Consequently, in this work, this approach is generalized, and firstprinciples electronic structure calculations were performed to investigate the effect of several electrode elements on the formation of charged point impurities in Mg_2Si and Mg_2Sn , within hybrid-density functional calculations. The calculation predictions for most of these electrodes were compared to experimental contacting results in order to establish the presented hybrid-DFT method as a reliable pre-selection tool for contacting electrodes. Experimental contacting results of Al, Cu, Ni, Ni₄₅Cu₅₅, Ti, and Zn, whether reported in previous literature or added in this work, are summarized in Section 5, and compared with predictions from hybrid-DFT calculations. Mg₂Si_{1,x}Sn_y was selected due to the high application potential of this material class, originating from the excellent TE properties of the n-type material, the abundance and environmental compatibility of the elements, and the technological maturity, demonstrated by several Mg₂Si_{1-x}Sn_x based TE modules.^[8a,14] Unless indicated separately, experiments were done using the 30:70 (Si:Sn) composition of the Mg₂Si_{1,x}Sn_y solid solution as it has the best TE performance and is, therefore, the most relevant practically.^[15] Twelve elements were considered as potential electrodes, representative of typical oxidation states: Ca and Zn for 2+, Al, In, Ga for 3+, Ti for 4+, the noble metals Cu, Ag, and Au, and the d⁸ metals Ni, Pd, Pt. Other transition metals are not considered because they generally have lower conductivity and higher oxidation states. The charged defect formation energies of the point impurities of all mentioned metals are compared to those of Bi, Sb, and Li in Mg_2X to check the possible occurrence of charge compensation in the n-type (Bi and Sb) and p-type (Li) doped material systems.

From the calculations, the most stable point defect induced by the studied metallic elements was predicted to be either electrically inactive, reduce the majority charge carrier density (charge trap), or (rarely) increase it (effective dopants), in dependence of the material system. Under Mg poor conditions, Ag, Au, Cu, Ga, and Zn act as electron traps with n-type Mg₂X (though Zn is inactive in n-type Mg₂Si), while Al, Ga, In, Ni (inactive in p-type Mg₂Si) and Ti acted as hole traps with p-type Mg₂X. Finally, comparisons between the results of both studies (calculations and experimental investigations) show a good agreement for a vast majority, which establishes the reliability of hybrid-DFT calculations in predicting potential interactions between TE materials and the electrodes of interest. Therefore, our method presents a powerful pre-screening tool to narrow down the pool of selection for potential electrodes, making experimental investigations more focused.

2. Experimental Section

2.1. Calculations

First-principles calculations were performed to study the defect properties of point impurities in Mg₂(Si,Sn) within hybrid density functional theory (hybrid-DFT).^[16] The generalized-gradient approximation exchange-correlation functional was used, parameterized by the Perdew–Burke–Ernzerhof (PBE), and the projector augmented-wave (PAW) pseudopotentials were used, as implemented in the Vienna Ab initio Simulation Package (VASP) code.^[17] The hybrid exchange correlation functional of HSE06 with the mixing parameter of 25% for the exact Hartree–Fock exchange and the screening parameter of 0.208 Å⁻¹ was used.^[16c]

The experimental lattice parameters were used throughout the study: 6.35 Å for Mg_2Si and 6.75 Å for Mg_2Sn .^[18d-f,19] The calculated band gaps for Mg_2Si and Mg_2Sn were 0.570 and 0.145 eV, respectively. The details of the calculation setting could be found in previous works.^[6a,13,20]

The defect structures were modeled as point impurities within the supercell approach. Instead of using the ternary compounds, the binary Mg₂X compounds were adopted. The defective supercell contains a single point impurity defect of *Me* in the 2 × 2 × 2 cubic Mg₂X supercell, where *Me* is one of following elements: Ag, Al, Au, Ca, Cu, Ga, In, Ni, Pd, Pt, Ti, and Zn representing possible contacting electrodes, Bi, Sb, and Li as typical dopants, and Mg and X as the native defects. High-symmetric oncentered configurations for extrinsic and intrinsic defects were considered, including interstitials (*Me*_{int}), impurity substitutional defects (*Me*_{Mg}, *Me*_X), vacancies (Mg_{vac}, *X*_{vac}), and antisites (Mg_X, *X*_{Mg}), where Me is the considered metal element.

To investigate the electronic structures and electric properties of impurity defects in Mg_2X , additional electrons or holes were added in the defect supercell, and the corresponding total energies of charged defects (D^q) were computed within the Jellium model. Thus, in total, the charged defect formation energies of 510 charged defect configurations in Mg_2X were calculated: 17 elements, three defect sites, five charge states, and two hosts (17 × 3 × 5 × 2). For these defect supercell calculations, the kpoint sampling with the Γ -centered 2 × 2 × 2 mesh grid was used. A kinetic energy cutoff of 296 eV was used for the plane wave basis set. Atomic structures were fully relaxed until the residual atomic forces were < 0.005 eV Å⁻¹.

For defect stability comparison, the formation energy (E_{form}) of a given defect *D* with a charge state *q* in Mg₂X was computed using the following equation.^[6a,20,21]

$$E_{\text{form}} \left[D^{q}, \text{ Mg}_{2}X, \mu_{i}, E_{F} \right] = E_{\text{tot}} \left[D^{q} \right] - E_{0} - \sum_{i} \mu_{i} \Delta n_{i} + qE_{F}$$
(1)

where $E_{tot}[D^q]$ and E_0 are the total energies of the defective and pristine supercells respectively, μ_i is the atomic chemical potential for a specific atomic element *i* in Mg₂X, Δn_i is the number difference of element *i* between the defective and pristine supercells, E_F is the Fermi energy of the electrons. The chemical potentials of Mg, Si, and Sn were computed considering Mg-rich or Mg-poor condition in the host Mg₂X. The atomic chemical potentials of the impurities were computed considering the reference solid phase under Mg-rich and Mg-poor condition (see Supporting Information).

Please note that here, "q" refers to the charge state of a given defective system used to characterize the ionization nature of the defect (whether it's a donor or an acceptor), which is distinct from the values of oxidation number or valence electrons associated with the impurity or defect. This integer "q" relates to the quantized electronic states, while the oxidation number or number of valence electrons pertain to the local distribution of charge density around a defect.

The defect density is approximately given by

$$n(D^{q}) = N_{0} \exp\left(-E_{\text{form}}/\kappa_{\text{B}}T\right)$$
⁽²⁾

where *T* is the considered equilibrium temperature (experimentally, in our case, it's the joining temperature), $\kappa_{\rm B}$ is the Boltzmann constant, $N_0 = n_{latt} \theta_{deg}$ is the total density of possible sites that can form a certain defect *D* with a charge state *q*, n_{latt} is the number density of available lattice sites and θ_{deg} is the number of degrees of internal freedom of a defect on a lattice site or the number of equivalent ways to form a certain defect at a particular site.^[20]

Note that DFT severely underestimates the band gap resulting in incorrect results for charged defect formation energies.^[20] To accurately describe the electrical properties of defects in narrow band gap thermoelectric materials such as Mg₂Si and Mg₂Sn, hybrid-DFT calculations were employed.

It is emphasized that the purpose of these calculations is investigating the charge compensation mechanism by electrode-related impurities, which goes beyond a dopant search study.^[22]

2.2. Experimental Procedure

In this work, n- and p-type $Mg_2Si_{0.3}Sn_{0.7}$ were synthesized using, respectively, Bi and Li as dopants. The nominal compositions were $Mg_{2.06}Si_{0.3}Sn_{0.665}Bi_{0.035}$ and $Mg_{1.97}Li_{0.03}Si_{0.3}Sn_{0.7}$, and the samples were synthesized following a powder synthesis and

 Table 1. Joining temperatures of the studied electrodes and literature reference for the experimental investigations.

Electrode	<i>T</i> [K]	Reference
	· join []	
Ag	723	Ayachi et al.[6a]
Al	723 & 773	Camut et al. ^[24]
Cu	873	Ayachi et al. ^[6b]
Ni	873 & 973	Pham et al. ^{[5c]*}
Ni ₄₅ Cu ₅₅	823	Ayachi et al. ^[6b]
Ti	923	This work
Zn	593	This work

 * The n-type sample studied in this paper was doped with Sb and had the composition $Mg_2Si_{0.385}Sn_{0.6}Sb_{0.015}.$

sample compaction procedure reported in previous works, leading to state-of-the-art TE properties.^[6b,15a,c,23] The obtained pellets were contacted with Ti and Zn foils following the contacting procedure utilized in Ayachi et al.^[6b] **Table 1** displays the different temperatures used for each electrode, whether tested in previous literature or presented as new data in this work. In all cases, the holding time was 10 min and the temperature increase rate was 1 K s⁻¹.

In the case of Ti, only contacting results with the p-type sample are presented, as contacting with n-type was not successful despite several trials under different conditions. In fact, in all cases, the n-type samples broke into pieces after contacting.

The successfully contacted pellets were cut and prepared for further investigations. Seebeck profile mappings were done using an in-house built Potential Seebeck Microprobe. To measure the Seebeck coefficient, a heated microprobe connected to a type T thermocouple placed on the surface of the sample heats a small volume around it, inducing a temperature gradient that generates a thermovoltage in the vicinity of the contact point. The Seebeck coefficient is then calculated using the temperature at the microprobe, the temperature at the heat sink, and two voltages picked up by the system as described in a previous work.^[25]

3. Results

3.1. Hybrid-DFT Calculation Results

In this section, hybrid-DFT calculations for point defects induced by the studied electrode materials in Mg-poor Mg₂Sn are summarized; the results for Mg-rich Mg₂Sn can be found in Supporting Information. This particular chemical potential condition was chosen as such because i) p-type samples are generally designed to be deficient in Mg,^[20,26] and ii) n-type samples can be expected to become Mg-poor under application conditions due to Mg loss,^[8a,27] even if they are initially designed to be Mg-rich. Calculations were also performed for Mg₂Si, but as most contacting experiments in the different literature were conducted with the Sn-rich Mg₂Si_{1-x}Sn_x with x = 0.6, 0.7 solid solution compositions, the focus in this work is on the calculation results for Mg₂Sn. Nevertheless, due to their technological relevance, the calculation predictions for Mg₂Si with all studied electrodes are given in Supporting Information. In all presented cases, the most stable electrode-induced defects were compared with the most stable intrinsic and relevant dopant-related defects (Bi and Sb as donors for n-type,^[15a] Li as an acceptor for p-type^[15c]), where the relevant defect is the one with the lowest formation energy, for example, interstitial or substitutional defect. Bi, Sb, and Li were chosen as they were reported in several studies to be effective dopants for n- and p-type conduction, respectively. An interpretation is then drawn based on the potential interplay between the most stable charged impurity defect and the assumed dopant defect. Considering only the defect with the lowest formation energy is an approximation based on the exponential weighting of the concentration of defects with different charges according to Equation 2.

For p-type samples, the Fermi energy ($E_{\rm F}$) area of interest is around the valence band maximum (VBM), while for n-type samples, it is around the conduction band minimum (CBM). Note that the most stable defect of a considered element generally depends on the atomic chemical potentials and the Fermi energy of the electrons, that is, it can differ between Mg-rich and Mg-poor, as well as for n- or p-type.

A general picture of the high-throughput investigations using all elements (Mg, Sn, Bi, Sb, Li, Ag, Al, Au, Ca, Cu, Ga, In, Ni, Pd, Pt, Ti, and Zn) is introduced, and the charged defect data are summarized in **Figure 1**, where the substitutional defects on Mg and X (Si or Sn) sites, the interstitial and vacancy defects are, respectively, referred to by "Mg", "X", "int", and "vac" subscripts. Out of these elements, Mg was included because of the high density of Mg vacancies (Mg_{vac}) in the Mg-poor Mg₂Sn system for both n- and p-type.^[20] Sn was also added to the comparative study because of the stability of Sn on Mg substitutional defect (Sn_{Mg}) in n- and p-type Mg₂Sn.^[20]

Figure 1a,b represents the charge state of the most stable defect for 15 impurities and two intrinsic defects in, respectively, n- and p-type Mg₂Sn under Mg-poor conditions. Each image is composed of two panels: the upper panel displays the formation energies of the considered point defects at $E_{\rm F} = E_{\rm CBM}$ for n-type and $E_{\rm F} = E_{\rm VBM}$ for p-type, and the lower panel displays a color coding of the charge state of each defect across the valence band, the conduction band, and the bandgap. The considered charge states are q = -2, -1, 0, 1+, 2+, and they are represented in red, orange, green, green-blue, and blue, respectively. When interpreting the n-type system, charges, and formation energies around the CBM need to be looked at, while when interpreting the p-type system, charges, and formation energies around the VBM are in focus. Each impurity can have several defect structures: substitutional at Mg, substitutional at X, and interstitial. Among them, only the lowest defect formation energy configuration is shown for the Fermi level at the relevant band extremum. For example, when $E_{\rm F}$ is at CBM, the Bi_X¹⁺ is the most stable charged Bi-related defect and Mg_{Vac}^{2-} is the most stable among the charged Mg defects. Similarly, for p-type, the formation energies under $E_{\rm F}$ at the VBM are compared for each impurity.

From Figure 1, it can be confirmed that Sb, Bi, and Li are in fact good dopants for Mg_2Sn , and that their doping efficiencies are high as they are shallow donors (Sb and Bi) and acceptors (Li). It can also be seen that Bi_x and Sb_x have very similar formation energies so they can be discussed in a combined manner. When interpreting the figure with respect to the potential impact of an electrode on the TE properties of Mg_2Sn , the formation energies,





Figure 1. Most stable charged defects of the studied elements: Mg, Sn, Bi, Sb, Li, Al, Au, Ca, Cu, Ga, In, Ni, Pd, Pt, Ti, and Zn in a) n-type and b) p-type Mg₂Sn under Mg poor conditions. In both material types, the upper panel represents the defect formation energies at a) $E_F = E_{CBM}$ and b) $E_F = E_{VBM}$, while the lower panel represents the different charge states of the studied defects across the energy range of interests. A dashed line in the upper panel indicates the formation energy of the relevant dopant for ease of comparison. In the lower panel, the subscripts refer to the type of defect: "X" refers to a substitutional defect on the X site of the Mg₂X system (in this case Sn), "Mg" refers to a substitutional defect on the Mg site, "int" refers to an interstitial defect, and "vac" refers to a vacancy defect.

and charge state need to be considered. Electrode-induced defects with formation energies comparable to that of the relevant dopant defect will lead to comparable defect densities, but defects that reduce the carrier concentration (compensating defects) will diminish the TE performance more than defects that increase it (additive defects) as zT(n) and efficiency $\eta(n)$ reduce more rapidly toward lower majority carrier concentrations.^[28] Thus, the most detrimental are defects with formation energies lower than the relevant dopant defect, with $q \leq -1$ at $E_{\rm F} = E_{\rm CBM}$ for n-type and $q \geq +1$ at $E_{\rm F} = E_{\rm VBM}$ for p-type. For this reason, the defect formation energies shown in Figure 1 are ordered according to their charge transition level from 0 (neutral defect) to -1 (electron compensating defect) in Figure 1a and 0 to +1 (hole compensating defect) in Figure 1b.

In n-type Mg₂Sn under Mg poor conditions as shown in Figure 1a, several impurities are stable with a negatively charged state, meaning that they act as electron traps. These defects are $Zn_{\rm Mg}, Au_{\rm X}, Ag_{\rm Mg}, Cu_{\rm Mg}, Ga_{\rm X}, Pt_{\rm X}, Li_{\rm Mg}, and Mg_{\rm vac}.$ Among these elements, looking at the formation energies at $E_{\rm F} = E_{\rm CBM}$, the order of expected defect densities is $Pt_X > Au_X > Li_{Mg} > Ag_{Mg} >$ $Zn_{Mg} > Ga_X > Cu_{Mg}$. Highly negative formation energies, like for Pt_x, indicate that instead of Mg₂Sn with a point defect, a new phase would be more stable and would form.^[29] This is a complexity that is not taken into account in this work, but can be understood by analyzing the defect formation energies calculated from a more suitable reference states with respect to these phases and not the atomic chemical potentials used in our hybrid-DFT calculations. $^{[30]}$ Among the shown defects, Ag_{Mg} and Zn_{Mg} are expected to cause the most charge compensation in the studied system as their formation energies, and therefore densities,^[20] are the closest to the main n-type dopants (Bi_x and Sb_x).

As for the other elements, Al_{Mg} , Pd_{int} , Sn_{Mg} , Ni_{int} , and Ca_{Mg} are inactive neutral defects because their charge at CBM is q = 0, while In_{Mg} and Ti_{Mg} are electron donor elements as their charges at CBM are positive (q = 1+ and 2+, respectively). However, with higher formation energies than the typical dopants and an additive effect the influence of In_{Mg} and Ti_{Mg} on TE properties and device performance will not be dramatic.

In p-type Mg_2Sn under Mg poor conditions as presented in Figure 1b, electron donor defects can occur with several ele-

ments, namely Sn_{Mg} , Ni_{int} , Pd_{int} , Al_{Mg} , In_{Mg} , Sb_X , Bi_X , Ga_{int} , and Ti_{Mg} . Out of these electron donors, Ga_{int} and Ti_{Mg} have a charge q = 2+ at when $E_{\rm F}$ is at VBM, while the rest has a charge q =1+. Looking at the formation energies of these defects when $E_{\rm F}$ $= E_{\text{VBM}}$, Sb_x, Bi_x are the two defects that are expected to cause a significant counter doping effect, which makes sense as Sb and Bi are both efficient n-type dopants. The other electron donor defects have relatively high formation energies, which predict that their influence on the charge carrier concentration of an Li-doped Mg₂Sn system will not be drastic. Similar to the case of Pt_x in ntype Mg₂Sn, Pd_{int} has a very low formation energy (≈ -1 eV), which also indicates the formation of a new phase. The other element-related defects $Au_{X}\text{, }Cu_{Mg}\text{, }Ag_{Mg}\text{, }Zn_{Mg}\text{, }and$ Ca_{Mg} are neutral around VBM, while Mg_{vac} and Pt_X are electron acceptors/hole donors, with charges q = -2 and -1, respectively. Mg_{vac} is already known as an intrinsic acceptor defect in the Mg₂X system and its effect on the charge carrier concentration is taken into consideration in several studies that developed efficient Li-doped Mg₂(Si,Sn) materials.^[15c,26c] As for Pt_x, here too its formation energy is strongly negative, which indicates again the formation of a new phase.

Table 2 summarizes the predicted effects of the presented electrodes with p-type (Li-doped) and n-type (Bi or Sb-doped) Mg₂Sn under Mg-poor conditions. The table is color-coded, where green indicates no expected effect from the electrode on the TE material, red indicates a predicted charge compensation causing a change in the carrier concentration, and gray indicates that the obtained calculated formation energies are strongly negative, indicating that a new phase would be formed between the TE material and the metal. The predictions were based on the following conditions, where no effect from the electrode is expected on the TE material if:

- The electrode-related defect is neutral
- E_{form} (electrode defect) > E_{form} (dopant) + 0.25 eV in case the electrode-induced defect is compensating the charge carrier concentration
- *E*_{form} (electrode defect) > *E*_{form} (dopant) in case the electrodeinduced defect adds carriers of the same type as the dopant

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Table 2. Summary of the predicted effect of the studied electrodes on Bi or Sb-doped (for n-type) and Li (for p-type) Mg₂Sn under Mg poor conditions.

Electrode	Predicted effect for the carrier concentration of		
	n-type Mg ₂ Sn	p-type Mg ₂ Sn	
Al	None	None	
Ag	Charge compensation	None	
Au	Charge compensation, possible formation of intermetallic phases	None	
Ca	None, possible formation of intermetallic phases		
Cu	Charge compensation	None	
Ga	Charge compensation	None	
In	None	Charge compensation	
Ni	None	None	
Pd	No effect, possible formation of intermetallic phases	Charge compensation, possible formation of intermetallic phases	
Pt	Charge compensation, possible formation of intermetallic phases		
Ti	None	None	
Zn	Charge compensation	None	

The usage of 0.25 eV as a threshold for the difference in formation energies $\Delta E_{\rm form}$ here is chosen based on the typical temperature range for the joining of the TE material and the electrode, as the actual defect concentrations will be close to the highest temperature experienced by TE material and electrode (if not equilibrated by long term annealing). If n_{Me} and n_{Dop} are considered the defect densities induced by the metal electrode and the dopant, respectively, their ratio (from Equation 2), approximately given by $n_{\rm Me}/n_{\rm Dop} \propto \exp\left(-\Delta E_{\rm form}/\kappa_B T\right)$, will be $\approx 0.8\%$ at T = 600 K and 4% at T = 900 K, which is the typical joining temperature range for this material system (see Table 1) and also encompasses the typical maximum operation temperature of this material system.^[8a,12,14a] Higher ΔE_{form} will therefore cause negligible changes in carrier concentration for typical sintering or operation conditions. For other material systems, different values might be considered for ΔE_{form} , depending on typical processing and operation parameters. Note that defects causing compensation are more detrimental than those causing additional carriers, therefore in this case no threshold is considered. Note that the prediction considers only thermodynamic equilibrium. For an effect to take place, diffusion in and out of the electrode is required

and therefore the speed with which the thermoelectric properties would change also depends on the defect mobilities; this was discussed in previous literature.^[6a]

4. Experimental Results

In the following, the experimental results for the contacting of Ti and Zn electrodes with Bi- and Li-doped Mg₂Si_{0.3}Sn_{0.7} are presented. Contacting results for other presented electrodes (Cu, Ni₄₅Cu₅₅, Ag, Ni, and Al) can be found in previous works by Ayachi et al., Pham et al., and Camut et al.^[5c,6a,b,24]

Figure 2 shows average Seebeck coefficient profile lines of n and p-type $Mg_2Si_{0.3}Sn_{0.7}$ contacted with Ti (shown in pink) and Zn (shown in blue). On each graph, the green-dashed line marks the Seebeck coefficient value of the TE material before contacting, and the light blue rectangles mark the metallic electrodes on both ends of the TE material. The measured Seebeck coefficient of the electrodes is represented in gray.

No change in the Seebeck value of the contacted sample was recorded for $Mg_2Si_{0.3}Sn_{0.7}$ joined with Ti at 923 K shown in pink in Figure 2b. The sample remained stable, despite high joining



Figure 2. Average Seebeck coefficient profile for (a) n- (Bi-doped) $Mg_2Si_{0.3}Sn_{0.7}$ contacted with Zn at 593 K, and (b) p- (Li doped) $Mg_2Si_{0.3}Sn_{0.7}$ contacted with Ti at 923 K (in pink) and Zn at 593 K (in blue). The green-dashed lines mark the Seebeck coefficient values of the TE materials before contacting, and the light blue regions indicate the metallic electrodes on both ends of the TE material.

temperature, and no effect from the electrode was observed. No contacting results of Ti with n-type $Mg_2Si_{0.3}Sn_{0.7}$ are provided due to constant sample breakage.

Contacting with Zn electrodes was done at 593 K on prepressed pellets. As can be seen from the blue graphs in Figure 2a,b, a change in the Seebeck profile was detected in the n-type sample but not in the p-type sample. The maximum value reached by *S* in the vicinity of the electrodes (x = 0 and x = 0.145 mm) is $-140 \ \mu V \ K^{-1}$. After a certain inward depth of ≈ 0.4 mm from each edge of the TE material, the Seebeck coefficient approaches that of the bulk TE material ($\approx -100 \ \mu V \ K^{-1}$). This non-homogeneous material change with a gradient toward the interface is a clear indication of an electrode-induced material change and the width of the changed layer can be employed to estimate diffusion coefficients.^[6a]

5. Discussion

In this section, the results obtained from hybrid-DFT calculations and experiments for Al, Cu, Ni, Ni₄₅Cu₅₅, Ti, and Zn are compared, and conclusions are drawn based on whether the results from both methods match or not. The comparative study for the case of Ag was already provided in one of our previous studies and therefore will not be repeated here.^[6a] The aim is to see if our hybrid-DFT calculations succeed in predicting what experimental results provide.

Experimental contacting results of Mg₂(Si,Sn) with Al were reported in previous works by Camut et al., showing an interesting trend in the Seebeck coefficient of the n-type samples.^[24,31] In fact, the TE material was joined with Al at 723 and 773 K and then annealed, and a systematic change in the Seebeck coefficient was observed in both cases. The change in S after contacting and annealing was larger for the samples joined at 773 K. A control experiment was also processed where a non-contacted n-type Mg₂Si_{0.3}Sn_{0.7} sample was annealed under the same conditions. Comparison of the results of both experiments led to the conclusion that the change in S is related to Mg loss due to its evaporation under high T and/or an interaction of the TE material with the electrode. For the p-type samples, no change in S was observed in either case, for annealed and non-annealed samples joined at 723 and 773 K. From a hybrid-DFT perspective, Al is not expected to cause any change in the charge carrier concentration of both Bi-doped and Li-doped Mg₂Sn samples under Mg poor conditions as discussed above. Therefore, in this case, though a clear match is reached between experiments and calculation predictions for p-type, the case of n-type is a bit more complex. In fact, the conclusion reached in the work of Camut et al. stated that the change in S is due to a combined effect of Mg loss—which would correspond to the effect of Mgvac in the defect picture—and Al "doping".[31] The difference in the extent of S change between the control experiment (non-contacted sample) and the contacted samples indicates such combined effect. However, in our provided defect formation energy picture, the most stable Al-related defect is a neutral defect, which means that no influence on the TE properties should be expected. A possible explanation is that the calculations are done for a pure Mg₂Sn matrix, while the real matrix is a solid solution. This would result in a difference in the bandgap value and therefore of the position of the CBM, which can affect the charge of the most stable state.

Moreover, as its charge transition level of neutral to negative is very shallow compared to the room temperature thermal energy, it can be easily ionized at above room temperature.

In previous literature from Ayachi et al., contacting n- $Mg_2Si_{0.3}Sn_{0.7}$ with Cu resulted in a change of the Seebeck coefficient of the TE material from -110 to $-160 \,\mu\text{V}\,\text{K}^{-1}$, and a further change up to $-230 \,\mu\text{V} \,\text{K}^{-1}$ was also recorded after annealing the contacted samples for 7 days at 723 K.^[6b,c,23a] Experiments using different sintering current conditions also resulted in the same behavior where S changed after contacting with Cu and changed further after annealing.^[6c] In all cases, no change in the Seebeck profile was recorded for the p-type samples, even after annealing. From a charged point defect perspective, it can be expected from Figure 1 that for highly doped n-type samples, a compensation of the charge carrier concentration is expected to occur due to the combined effect of the Mg_{vac} and Cu_{Mg} defects. Such compensation of the charge carriers translates experimentally in a change in the Seebeck coefficient and the electrical conductivity. In this case, the predictions of the hybrid-DFT calculations successfully explain the experimental behavior. Such a match between calculations and experiments is also reached for the p-type samples, as the most stable Cu-related defect is a neutral defect. Therefore, no influence on the carrier concentration is expected to occur, which is the case experimentally, as no change in S of p-type samples was detected.

Hybrid-DFT predictions are compared with the experimental results reported in Pham et al. to study the Ni electrode case.^[5c] In said work, contacting of n- and p-type $Mg_2Si_{1-x}Sn_x$, x = 0.6-0.7 with Ni at 873 and 973 K was reported. Results showed no change of the TE properties of the n-type samples after joining at both temperatures. As for the p-type samples, no change in the TE properties was observed after joining at 873 K as the average *S* along the sample remained $\approx 90 \ \mu V \ K^{-1}$, which is the precontacting value. However, for contacting at 973 K, a change in the properties was recorded. This S change could be explained by the high joining temperature, which could have affected the TE properties of the sample.^[27c] Also, as contacting at 973 K was done on powder and not pre-pressed pellets, the combined sintering and joining experiment could have resulted in non-optimized TE properties of the sample. In summary, it is possible to claim that the hybrid-DFT predictions match with the experimental data for both n- and p-type cases, as the defect formation energy calculations under the studied conditions revealed that the most stable Ni-related defects had much higher formation energies than the intrinsic and main dopant defects. This means that no effect is expected to occur from the Ni electrode on the TE properties of the Sn-rich Mg₂(Si,Sn) system, which is what was observed experimentally for 873 K.

Experimental contacting results of Bi-and Li-doped $Mg_2Si_{0.3}Sn_{0.7}$ with $Ni_{45}Cu_{55}$ were reported in Ayachi et al.^[6b] A behavior similar to the contacting with Cu was observed, where the Seebeck value of the n-type samples changed after joining from -110 to $-160 \ \mu V \ K^{-1}$, while no such change was observed for p-type samples. Hybrid-DFT calculations show that when looking at the Ni and Cu defects in the Bi-doped Mg_2Sn system under Mg-poor conditions, only the Cu-related defects are expected to be stable enough to cause a significant change of the charge carrier concentration. This means that, from a defect perspective, the alloy $Ni_{45}Cu_{55}$ electrode is expected to behave

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Figure 3. Schematic tables of elements summarizing the contacting experimental results and the calculation predictions for all studied electrodes for a) n-type Mg_2Sn and b) p-type Mg_2Sn . Each element cell is diagonally divided in two, the upper triangle providing information on the experimental data and the lower triangle on the calculation predictions. The cells are color coded as explained in the legend on the right-hand side of the tables.

similarly to the Cu electrode, under the approximations set in this study. Charge compensation is then predicted in n-type samples but not in p-type samples, which is what is reported in previous literature.^[23a] Based on these results, it is possible to establish a match between the results of the joining experiments and the predictions from the hybrid-DFT calculations for the case of Ni₄₅Cu₅₅. This encouraging result indicates that possibly even alloys can be pre-assessed as electrodes by analyzing the point defects of the constituting elements, which are much easier computed.

Contacting p-type $Mg_2Si_{0.3}Sn_{0.7}$ with Ti showed an unchanged Seebeck profile for the joined sample. This matches the predictions of the hybrid-DFT calculations that showed that the most stable Ti-related defect has a high formation energy to influence the charge carrier concentration, hence the TE properties.

Finally, contacting experiments with Zn resulted in a change of the TE properties, hence the charge carrier concentration, of the n-type samples but not the p-type samples. Zn contacting was also presented in a recent work from Camut et al. where it was used as a sputtered diffusion barrier for Al contacting on Mg₂Si_{0.3}Sn_{0.7} ($T_{\text{join}} = 723$ K).^[24] In said literature, the n-type samples showed a gradient in the Seebeck profile, even though the layer of the sputtered Zn was only 8 µm thick. No gradient was observed with p-type samples. In our work, Zn was joined as a

foil of 250 μm thickness at 593 K, and here too, a gradient was observed in the contacted n-type sample only. The predictions from the hybrid-DFT calculations show that Zn is expected to cause a change in the carrier concentration of n-type through a charge compensation between the $Zn_{\rm Mg}$ and $Bi_{\rm Sn}$ defects. No such charge compensation is expected to occur for the p-type samples. In this case as well, a good match is reached between experimental results and calculation predictions.

Figure 3 represents two tables of elements summarizing the available contacting experimental results and the hybrid-DFT calculation predictions. The upper table represents n-type Mg₂Sn while the lower table represents p-type Mg₂Sn, and both tables are truncated to highlight the elements of interest. In both tables, the main lattice elements (Mg and Sn) are marked in purple, while the doping elements (Li, Bi, and Sb) are marked in yellow. The other 12 elements are color-coded according to the experimental and calculation results. Each element cell is diagonally divided in two, the upper triangle showing the results of the experimental investigations, and the lower triangle showing the hybrid-DFT data. Red color coding indicates that the electrode element causes (or is expected to cause) a charge compensation in the TE material, while green indicates no charge compensation. If both halves of a cell match in color, it is a match between experiments and calculations. Blue indicates the formation of an intermetallic phase as explained in the results section under Figure 1 and gray indicates that no experimental investigations were performed. Elements written in black are elements with their most relevant defect being an electron donor, elements written in white have their most relevant defects as electron acceptors, and underlined elements are neutral defects.

In the case of the elements where both experiments and calculations were done, namely Ag, Al, Cu, Ni, Ti, and Zn, it can be seen that for n-type Mg_2Sn a good match is reached for Ag, Cu, Ni, and Zn, and only for Al more detailed calculations or further experimental work might be necessary. On the other hand, for p-type Mg_2Sn , a good match is reached for all six electrodes. It can therefore be concluded that, despite the approximations taken, agreement is obtained between almost all of the experimental studies and the corresponding hybrid-DFT calculation predictions.

Our electrode pre-selection is based on the comparison of point defect formation energies with respect to specific dopants (Bi/Sb and Li); however, the conclusions are general: if a less effective dopant is employed, the predicted effects will be the same, but potentially more pronounced (if the dopant is more relevant than intrinsic defects). If a more effective dopant was employed the effects will still be the same, only weaker. However, the Mg₂X system has been intensively studied and Li and Bi/Sb are the best so far reported dopants.^[30,32]

6. Conclusion

In this work, first-principles hybrid-density functional calculations are investigated as a potential pre-selection tool for contacting electrodes. To this end, the charged defect formation energies for several electrode materials (Al, Au, Ca, Cu, Ga, In, Ni, Pd, Pt, Ti, and Zn) in Li, Bi, and Sb-doped Mg₂X systems were calculated. The calculation predictions for Mg-poor Mg₂Sn were compared to experimental data of Sn-rich Mg₂X. Based on the obtained comparisons between hybrid-DFT calculations and experimental investigations, a good match between both methods was reached in all but one of the studied cases. It needs to be emphasized that this agreement is reached despite a number of simplifications, necessary to be able to make this comparison: first, the details of the potentially complex interface microstructure that will form during contact making is not directly considered; second, kinetic aspects are not required for the analysis (based on the argument that for long-lasting TE devices, thermodynamic equilibrium is a good indicator), and third, good predictability is achieved for experimental data of solid solutions based on calculations for the binaries. This is practically highly relevant as most high-performance TE materials are solid solutions. The approach can also be extended naturally to alloys as electrode materials. These are partially employed practically and can plausibly be covered by calculating the defect formation energies of the individual species (as done here for CuNi) and considering the changed atomic chemical potential.

In conclusion, we have shown that our proposed firstprinciples hybrid-density functional calculation method is a practically feasible and reliable method to predict the interplay between the electrodes and the TE materials of interest. This facilitates electrode pre-selection, makes contact design more efficient, and thus helps to transfer TE material progress into device enhancement.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

contacting, defects, hybrid-DFT, interface design, thermoelectrics

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