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Thermoelectric and Electrical Transport Properties of Mg$_2$Si Multi-doped with Sb, Al and Zn

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Enhanced thermoelectric and electrical transport properties of Mg$_2$Si-based thermoelectric materials have been achieved by multi-doping with Sb, Al and Zn. Results on the investigation of the electrical transport and thermoelectric properties of multi-doped samples prepared using the spark plasma sintering technique are reported. Synchrotron radiation powder x-ray diffraction was used to characterize the structures of the doped samples. The electrical transport properties were determined from mid-infrared reflectivities, Hall effect and conventional quasi-four probe conductivity measurements. Using the electron concentrations ($N$) determined from the Hall coefficients, the effective masses ($m^*$) were calculated from the frequency of the plasma edge ($\omega_p$) of the infrared reflectivities. The thermoelectric performance and thermoelectric figure of merit (ZT) 300 K to 900 K of the doped Mg$_2$Si compounds were calculated from the measured temperature dependent electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and thermal conductivity ($\kappa$). A maximum ZT of 0.964 was found in Sb0.5%Zn0.5% doped Mg$_2$Si at 880 K. This value is comparable to the PbTe based thermoelectric materials.

In 2010, Mg$_2$Si$_{1-x}$Sn$_x$ was doped with Li and Ag was investigated by Isoda et al.$^{12}$ Compared to the single-doped samples, in double-doped Mg$_2$Si$_{1-x}$Sn$_x$ with Li (20000 ppm) and Ag (5000 ppm) the Seebeck coefficients have increased and maximized to 250 $\mu$VK$^{-1}$ at 500 K. The previous Seebeck coefficients were found to be positive, indicating p-type doping with holes as conduction carriers. In comparison with single Li-doped Mg$_2$Si, double doping increased the carrier concentration to more than double.$^{13}$ In 2011, Sb doped Mg$_2$Si$_{1-x}$Sn$_x$ compound was synthesized and the peak power factor of the sample reached $3.2 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$ at 610 K with a maximum ZT >0.9, comparable to PbTe based thermoelectric materials.$^{14}$ In addition, Du et al. reported a maximum ZT of 0.85 was obtained at 700 K for Mg$_2$(Sb$_{0.01}$Sn$_{0.6}$)$_{1-x}$Sb$_{0.03}$ for $x=0.01$, and found that the carrier concentration and electrical conductivity were significantly enhanced by the Mg in the interstitial sites.$^{15}$ Moreover, Liu et al. also found high thermoelectric performance Mg$_2$(Sb$_{0.11}$Sn$_{0.45}$)$_{0.53}$Sb$_{0.03}$ with a maximum ZT of 1.0 at 725 K for $x=0.08$ and a carrier concentration 1.9$\times 10^{20}$ cm$^{-3}$.$^{16}$ Khan et al. reported that an even higher figure of merit (ZT) of 1.4 can be obtained at 800 K for multi-doped compound of Mg$_2$Si$_{1-x}$Sn$_x$ with Bi.$^{17}$ Le-Quoc reported Hall effect measurements at room temperature on a thin film of Sb doped Mg$_2$Si$_{1-x}$Sn$_x$ (x=0.4, 0.5, 0.6) and showed that Sb acted as electrons donors but the carrier concentration increased non linearly with the Sb content. The electrical conductivity of the Sb doped films, however, is still low with a charge carriers concentration less than 10$^{19}$ cm$^{-3}$.$^{18}$ In 2014, a significant enhancement of the thermoelectric figure of merit of Mg$_2$Si to 0.7 at 873 K was...
achieved by double-doped with a combination of Bi, Pb, and Sb. It was observed that the addition of any two of the doping elements can increase the electrical conductivity due to the excess free electrons in the conduction band. For example, Jiang et al. found the thermoelectric performance was improved by introducing three types of point defects, Sb dopants, Mg vacancies, and Mg interstitials, in MgSbSi0.75Sb0.25 samples. Isoda et al. found the highest ZT value in an Al/Sb double-doped MgSi0.75Sb0.25 of 0.94 at 850 K. Therefore, Sb is considered to be an effective dopant to increase the carrier concentration. Previous studies have shown that double or multi-doping is a promising approach to further enhance the thermoelectric figure of merit (ZT) in MgSbSi-based thermoelectric materials.

The objective of this paper is to characterize and to better understand the effect of multi-dopants on the host lattice of MgSbSi crystal. For this purpose, Sb, Al, and Zn multi-doped MgSbSi samples were synthesized by spark plasma sintering technique. The electrical transport properties were studied by mid-infrared reflectivity measurements. Since the reflectivity is related to the dielectric function, frequency dependent optical conductivity can be extracted from the analysis. Static (dc) conductivity is obtained by extrapolation to zero photon energy. In addition, electrical resistivity and Hall coefficient were also measured with conventional quasi-four-probe method. Thermoelectric properties of the multi-doped MgSbSi samples were determined from the temperature dependency of the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). The figure of merit (ZT) and power factor (S²σ×T) of Sb, Al, and Zn multi-doped MgSbSi samples were then calculated.

The layout of the paper is as follows. First, details on the experimental procedure will be described. The diffraction patterns of multi-doped MgSbSi are compared with pure MgSbSi. This is followed by a discussion on the electrical properties extracted from mid-IR reflectivity and conventional quasi-four probe method. Finally, the thermoelectric properties were characterized from results on the temperature dependent of Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). The figure of merit (ZT) and power factor (S²σ×T) were calculated and discussed.

Experimental details

Synthesis and Sintering Process for Doped MgSbSi Samples Preparation

Crystal growth of polycrystalline MgSbSi was performed using an electric furnace by lowering the temperature from slightly beyond the melting point (1378 K) of MgSbSi, and was initiated from stoichiometric melts with Mg : Si = 2 : 1. The starting materials, Mg, Si were placed in an alumina crucible under argon-hydrogen forming gas (0.08Mpa). Intentional impurities of antimony (Sb) and aluminium (Al), and an isoelectric impurity of zinc (Zn) were incorporated in order to increase the electronic carrier concentrations and phonon scattering. The Sb and Al dopants predominantly substitute to Si and Mg, respectively, which act as donors, and Zn is expected to show isoelectric characteristics at Mg site, i.e., no contribution to carrier generation but an influence over phonon behaviour, bringing about reduction in thermal conductivity. These donor and isoelectric dopants were incorporated during the all-molten synthesis process at 1378 K, and the resultant polycrystalline MgSbSi was pulverized to powder with a size of 25-75μm, then placed into a graphite die and sintered by a plasma-activated sintering (PAS) technique using an ELENIX Ed-PAS-III-Es. The sintering was basically performed at 1123 K for 10 min. with a pressure of 40 MPa in an Ar (0.06 MPa) atmosphere and the sintering temperature and time were varied depending on the type of dopant that was used to obtain a dense material. The compositions of the samples were analyzed by electron-probe microanalysis (EPMA) using JEOL JXA-8900. The concentration of the dopant impurities in the samples was estimated by grow discharge mass spectrometry (GDMS) using V.G.Scientific VG-9000.

Powder X-ray Diffraction Measurement

Powder MgSbSi from Alfa Products with a purity of 99.5%. MgSbSi was doped with nominal 0.5 at. % of Sb, 0.5~1.0 at. % of Al, 0.5~1.0 at. % of Zn by the spark plasma sintering technique. The four materials studied were MgSbSi with nominal at. % of Sb0.5%, Al0.5%, Zn0.5%, Sb0.5% Al1%, Sb0.5% Zn0.5%, and Sb0.5% Zn1.0%. Synchrotron X-ray diffraction experiments on the pure standard and doped MgSbSi samples were performed at CMCF-II, Canadian Light Source (CLS), using synchrotron radiation (λ=0.68880 Å). The diffraction patterns were analyzed using the JANA 2006 software package with the lattice parameters determined by Le Bail fit.

Mid-Infrared Reflectivity Measurement

Mid-infrared normal-incidence reflectance spectra on pure and Sb Zn Al multi-doped MgSbSi samples were measured at the side-station of the U2A beamline, National Synchrotron Radiation Facility, Brookhaven National Laboratory. Mid-infrared spectra were recorded on a Bruker Vertex 80v FTIR spectrometer and a Hyperion 2000 IR microscope attached with a liquid nitrogen cooled HgCdTe detector. Powder samples were prepared and placed the 300 μm culet of a Sintek mini type lida diamond anvil cell. After loading the sample the DAC is closed with hand compression to flatten the powder sample. After re-opening the DAC, one half of the flattened sample was removed leaving half of the clean diamond face exposed. In this way, the orientation of the sample surface and diamond support is ensured to be the same. This is critical for the conversion of the reflectance to absolute reflectivity. The procedure is as follow, the reflectance of diamond phase (I0) and the sample (Iw) were measured. The reflectance of the sample was then converted to absolute reflectivity by normalization to the reflectance of the diamond surface. From the known reflectivity of diamond, the reflectivity of sample-air interface (Rw) was calculated as Rw=(lw/I0)×(I0/Iw), where lw/I0 is a constant of 0.185. All the
spectral data were collected at a resolution of 4 cm\(^{-1}\) and accumulated for 512 scans.

Frequency dependent optical conductivity was obtained by Kramers–Kronig (K–K) analysis of the reflectivity data by fitting with a variational K–K constrained dielectric function, implemented in the RefFIT code.\(^{24,25}\) The frequency dependent optical conductivity was derived from the fit to a Drude–Lorentz (DL) model and the dc conductivity obtained from extrapolation to zero frequency.

Electrical Transport Properties and Thermoelectric Properties Measurements

Polycrystalline Mg\(_2\)Si fabricated by an all-molten synthesis method was used as the source material. The Sb, Al and Zn dopants were incorporated during a melt synthesis process at 1378 K, and the resultant polycrystalline Mg\(_2\)Si was pulverized to powder with a size of 25~75μm, then placed into a graphite die and sintered by a plasma-activated sintering (PAS) technique using an ELENIX Ed-PAS-III-Es. The sintering was performed at a pressure of 40 MPa in an Ar (0.06 MPa) atmosphere and the sintering temperature and time were varied depending on the type of dopant that was used to obtain a dense material. The temperature-dependent thermoelectric properties were measured using an ULVAC-RIKO ZEM2 to determine the Seebeck coefficient and the electrical resistivities, and an ULVAC-RIKO TC-7000H to determine the thermal conductivity over a temperature range from 300 K to 900 K. Electrical resistivity below room temperature was measured by the standard four-probe method in a commercial Quantum Design Physical Property Measurement System (PPMS) (1.8K T 400K, 0 H 70kOe). Hall effect was measured at fixed temperature by changing the magnetic from -5T to 5T.

Results and Discussion

High resolution synchrotron angle dispersive X-ray diffraction patterns of pure Mg\(_2\)Si, Mg\(_2\)Si doped with Sb0.5%Al0.5%Zn0.5%, Sb0.5%Al1.0%, Sb0.5%Zn0.5%, and Sb0.5%Zn1.0% were measured with photon of 18 KeV (λ=0.68880 Å) on the CMCF-II beamline Canadian Light Source Inc. at room temperature, (Fig. 1) The lattice constants were determined from full profile Le Bail fit to the diffraction patterns from 5\(^{\circ}\) to 40\(^{\circ}\) using the JANA 2006 package. The X-ray diffraction pattern of pure Mg\(_2\)Si can be indexed readily to the cubic anti-fluorite (CaF\(_2\)) structure with space group \(Fm\)-\(3m\). In increasing diffraction angle, the miller indices (hkl) of the Bragg peaks are identified as (111), (200), (220), (311), (222), (400), (331), (420), (422), (511), (440), (531) and (600) reflections. The diffraction patterns of Mg\(_2\)Si doped with Sb, Zn and Al all share the same profile to pure Mg\(_2\)Si except the Bragg peaks have shifted noticeably to lower angles. The observation indicated that even with a small dopant concentration (0.5%~1.0%) the cubic lattice of Mg\(_2\)Si is expanded. Fig. 2 (a) and (b) summarize the experimental lattice parameters and unit cell volumes for pure Mg\(_2\)Si and doped Mg\(_2\)Si. The cubic cell parameter of pure Mg\(_2\)Si \(a=6.2843(9)\) Å is increased to 6.3506(9) Å to 6.3634(9) Å by the addition of the dopants (Zn, Al, Sb). This can be rationalized as the atomic sizes of Zn, Al dopants are larger than Mg, and Sb, which replace the Si, also has a bigger size. We can conclude unequivocally that the cubic cells of all the doped samples are larger than pure Mg\(_2\)Si. The observations also lend support to the expectation that Al and Zn dopants will occupy the Mg sites, while Sb replaced Si in the Mg\(_2\)Si crystal structure. If this is the case, Al, Zn, and Sb doped Mg\(_2\)Si are an n-type semiconductors. As will be shown latter, this assignment is in agreement with the negative Hall coefficients.

![Fig. 1. Angle dispersive x-ray diffraction patterns of pure Mg\(_2\)Si and doped Mg\(_2\)Si measured at room temperature.](image-url)
Infrared reflectivity experiment can provide information on the electrical transport of a material. Mid-infrared reflectivity spectra were measured with an internal Globar radiation source (600 cm$^{-1}$-8000 cm$^{-1}$) installed at the U2A beamline on pure Mg$_2$Si and Mg$_2$Si multi-doped with Sn Zn and Al. The electronic transport properties of the doped samples were extracted. The experimental reflectivities for pure and multi-doped Mg$_2$Si are compared in Fig. 3. The infrared reflectivity of all the doped Mg$_2$Si samples exhibit a Drude-like behavior at low frequency indicative of doped semiconductor. In comparison, the un-doped Mg$_2$Si sample does not have the free electron-like feature, indicating it is a semiconductor with a small band gap. This is to be expected as Mg$_2$Si is a semiconductor with a small indirect band gap of 0.6 eV.$^{27}$ In comparison to the flat and featureless reflectivity of pure Mg$_2$Si, the reflectivities of the multi-doped samples extrapolated to zero frequency are much higher. Note that a good conductor, such as copper or aluminum, has a reflectivity close to unity at zero frequency.

The Sb, Zn, Al-doped Mg$_2$Si samples show a common feature in the reflectivity curves around 1800 cm$^{-1}$. It is the appearance of a “dip” in the spectra. The minimum in the reflectivity is characteristic of a doped semiconductor and is known as the plasma reflection edge or plasma dip.$^{28}$ According to the simple Drude model, the energy at the energy minimum (plasma frequency $\omega_P$) is related to the carrier concentration ($N$) and the effective mass ($m^*$), $\omega_P^2 = \frac{N e^2}{\varepsilon \varepsilon_0 m^*}$ where $\varepsilon$ is the dielectric constant of the material.
and $\varepsilon_0$ is the vacuum permittivity. Therefore, the effective mass ($m^*$) of a doped semiconductor can be extracted from the plasma frequency ($\omega_p$) provided the electron concentration ($N$) is known. Detail results will be reported, analyzed and discussed below.

The frequency dependence conductivity, the optical conductivity, can be obtained by performing a Kramers–Kronig (K–K) analysis on the reflectivity data. The procedure is as follow, the optical conductivity obtained from a variational K–K transformation is fitted to a Drude-Lorentz (DL) model and the $dc$ conductivity is estimated by extrapolation to zero frequency. A comparison illustrating the quality of the fit is shown in Fig. 5. In the figure, the raw and fitted infrared reflectivity spectra of 0.5% Sb&0.5% Zn doped Mg$_2$Si sample are compared. The $dc$ conductivities of the doped samples obtained with this procedure are reported in Table I. The Mg$_2$Si: Sb0.5%Zn1.0% sample is found to have the highest $dc$ conductivity of 767 S cm$^{-1}$ and an extrapolated reflectivity of $\sim$0.73 at zero frequency. The trend of the dc conductivities extracted from infrared reflectivity agree qualitatively with bulk electrical measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_0$ (S cm$^{-1}$)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Si: Sb0.5%Al0.5%Zn0.5%</td>
<td>507</td>
<td>3.72 x10$^{-14}$</td>
</tr>
<tr>
<td>Mg$_2$Si: Sb0.5%Al1.0%</td>
<td>627</td>
<td>3.94 x10$^{-14}$</td>
</tr>
<tr>
<td>Mg$_2$Si: Sb0.5%Zn0.5%</td>
<td>480</td>
<td>3.77 x10$^{-14}$</td>
</tr>
<tr>
<td>Mg$_2$Si: Sb0.5%Zn1.0%</td>
<td>767</td>
<td>5.57 x10$^{-14}$</td>
</tr>
</tbody>
</table>

The static $dc$ conductivity increased dramatically from pure Mg$_2$Si, due to the larger concentration of free electrons in the conduction band by doping with Zn, Al, and Sb. From the free electron model, $dc$ conductivity is proportional to the electron concentration ($N$), and scattering time ($\tau$). The electron scattering time ($\tau$) is a parameter in the Drude-Lorentz model and can be obtained from the fitting of the reflectivity data. The fitted relaxation times of doped Mg$_2$Si samples are tabulated in Table I. The derived relaxation times of ca. 10$^{-14}$ sec. is consistent with other doped semiconductors. The electron concentration ($N$) in a doped semiconductor is the density of the mobile electrons or holes, (n- or p- doped). Since the host crystal Mg$_2$Si is the same for all samples, the $dc$ conductivity depends only on the nature of the dopants. The dramatic enhancement of the $dc$ conductivity by the dopants is due to the occupation of the free electron-like conduction bands. In spite of the simplicity of the Drude-Lorentz model and the neglect of low frequency (<600 cm$^{-1}$) absorption which is not accessible by mid-infrared radiation, the results indicate that the $dc$ conductivity can be improved by addition of the (Zn Al Sb) dopants.

Table I. Summary of $dc$ conductivity ($\sigma_0$) & carrier relaxation time ($\tau$) of doped Mg$_2$Si.

Although the trend of increasing electrical resistivity and reflectivity is the same from IR reflectivities and four-probe conductivity measurements, the comparison of the absolute magnitude is less satisfactory. (Fig. 6) The $dc$ conductivities derived from infrared reflectivity has the same order of magnitude as the bulk measurements, but are approximately four times smaller. One contributing factor may be the infrared beam only surveyed a very small region (20×20 μm$^2$) within a couple of microns into the sample surface. This is different from the quasi-four-probe conductivity method which is a bulk sensitive technique. At the sample surface the atom density is less than the bulk and the chemical bonding in the surface is also stronger. Therefore, there are less free electrons near the sample surface thus reducing the electrical conductivity. Although plausible, this effect cannot satisfactorily explain the discrepancy observed here. Since the $dc$ conductivity was obtained from the extrapolation of the frequency dependent conductivity to zero frequency, it is not certain if the omission of reflectivity at very low energy (i.e. < 600 cm$^{-1}$) may have an effect. From past experience, we expect the $dc$ conductivity derived from an IR measurement should agree within an order of the magnitude of the value obtained from the bulk technique. We found no systematic error in the experiment and on the treatment of the data. In a previous study, we have also compared the $dc$ conductivity derived from IR reflectivities to bulk measurements on doped Mg$_2$Si and the agreements were favorable. We suspect the most likely source of the disagreement may be related to a precise knowledge on the concentration of the dopants. The doped samples used in this study were synthesized by plasma spark sintering method. It is very difficult to control the precise stoichiometry. Another possible source of the discrepancy may be due to non-uniform distribution of dopants in the sample. In a study of Sb and Bi doped-Mg$_2$Si, it was found by high resolution transmission microscopy (TEM) that due to the limited solubility excess Sb and Bi atoms are present in the grain boundaries that may enhance the conductivity of the bulk sample. In comparison, IR measurements only examine...
a very small spot of ca. 20×20 μm² of the sample so this may produce different results. Finally, the formation of a thin oxide layer on the surface may also contribute to the lower conductivity derived from the IR experiments. A careful characterization of both samples is critical to resolve the discrepancy.

The bulk electronic transport properties of the Zn, Al, Sb multi-doped Mg₃Si samples were determined by temperature dependent electrical resistivity and Hall coefficient with the quasi-four-probe method. The temperature dependent electrical resistivities (ρ) of doped Mg₃Si samples (Fig.4) were measured with a current of 3 mA and sectional areas between 1.05×0.78 mm² ~ 1.45×1.01 mm². It is found that the electrical resistivity of Mg₃Si: Sb0.5%Al1.0% increased from 300 μΩ cm to 500 μΩ cm from 10 K to 300 K. At 300 K, the electrical resistivity in Mg₃Si: Sb0.5%Zn1.0% is smaller than the other doped samples of 430~500 μΩ cm. The results suggest that there are more free electrons in the conduction band of the other samples leading to higher electrical conductivity. Comparing Mg₃Si: Sb0.5%Zn0.5% and Mg₃Si: Sb0.5%Zn1.0%, the electrical resistivities were found to decrease with concentration of the Zn dopant. Since the concentrations of Sb were the same in these two samples and the Zn atoms were expected to occupy the Mg sites, this conductivity trend suggests there are more mobile electrons in the conduction band with more Zn dopants.

![Fig. 7. Hall coefficients (R_H) of doped Mg₃Si samples were measured by quasi-four-probe method.](image)

The measured Hall coefficients (R_H) of Zn, Al, Sb-doped Mg₃Si samples are shown in Fig. 7. The negative and almost constant Hall coefficients show the multi-doped Mg₃Si materials are n-type doped semiconductors. Using the equation N=1/(eR_H), where e is the electron charge, and R_H is the Hall coefficient) the electron concentrations (N) were calculated and show in Table II. Possibly, Mg₃Si: Sb0.5%Al1.0% has the largest electron concentration (N) of 1.78×10²⁰ cm⁻³, due to the high doping concentration. The electron concentration (N) of the multi-doped Mg₃Si samples of ca.10²⁰ cm⁻³ are in reasonable agreement with that estimated from the free electron model. Therefore doped-Mg₃Si are doped semiconductors. The results are supported by the low plasma frequencies of the doped samples. The low plasma frequencies observed in the IR region is also indicative of a doped semiconductor.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R_H (cm²/C)</th>
<th>N (cm⁻³)</th>
</tr>
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<tbody>
<tr>
<td>Mg₃Si: Sb0.5%A1.0%Zn0.5%</td>
<td>-5.53×10⁻²</td>
<td>1.17×10¹⁰</td>
</tr>
<tr>
<td>Mg₃Si: Sb0.5%A1.0%</td>
<td>-3.50×10⁻²</td>
<td>1.78×10¹⁰</td>
</tr>
<tr>
<td>Mg₃Si: Sb0.5%Zn0.5%</td>
<td>-4.33×10⁻²</td>
<td>1.44×10¹⁰</td>
</tr>
<tr>
<td>Mg₃Si: Sb0.5%Zn1.0%</td>
<td>-3.75×10⁻²</td>
<td>1.67×10¹⁰</td>
</tr>
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</table>

Table II. Summary of electron concentration (N) calculated from Hall coefficient (R_H) of doped Mg₃Si.

The effective mass can be calculated from the plasma frequency observed in the infrared reflectivity and the electron concentration from the Hall coefficient. The plasma frequency ω_p is related to the electron concentration (N) and the effective mass (m*) by ω_p² = ne²/εₑε₀m*, where εₑ is the dielectric constant of the material, and ε₀ is the vacuum permittivity. Therefore, the effective mass (m*) is inversely proportional to the square of plasma frequency (ω_p). Assuming a constant optical dielectric constant (ε) of 12.82 for doped Mg₃Si samples, the effective masses were calculated for all the doped Mg₃Si samples studied. As shown in Table III, the effective masses of doped Mg₃Si samples are between 0.255mₑ and 0.361mₑ, where mₑ is the mass of a free electron. The light effective masses found in this work are comparable with previous measurements listed in Table IV. Electrons with lighter effective mass are easier move in the conduction band and therefore contribute to a higher electrical conductivity. The light effective masses i.e. 0.255mₑ to 0.361mₑ of doped Mg₃Si show occupation of free-electron-like conduction band by the excess electron donated by the dopants.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ω_p (cm⁻¹)</th>
<th>m*/mₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₃Si: Sb0.5%A1.0%Zn0.5%</td>
<td>1791</td>
<td>0.255</td>
</tr>
<tr>
<td>Mg₃Si: Sb0.5%A1.0%</td>
<td>1899</td>
<td>0.346</td>
</tr>
<tr>
<td>Mg₃Si: Sb0.5%Zn0.5%</td>
<td>1788</td>
<td>0.316</td>
</tr>
<tr>
<td>Mg₃Si: Sb0.5%Zn1.0%</td>
<td>1798</td>
<td>0.361</td>
</tr>
</tbody>
</table>

Table III. Summary of effective mass (m*) of doped Mg₃Si calculated from the plasma frequency (ω_p) within the infrared reflectivity.

To define the thermoelastic properties of doped Mg₃Si samples, the temperature dependent electrical conductivity (σ), Seebeck coefficient (S), power factor (σ²S²T), thermal conductivity (k) were measured up to 900 K, and the
corresponding figure of merit (ZT) were calculated. As shown in Fig. 8 (a)-(e), the electrical conductivity of doped Mg$_2$Si decrease from $2.5 \times 10^5$ S m$^{-1}$ to $0.8 \times 10^5$ S m$^{-1}$ when the temperature is raised from 300 K to 900 K. The highest electrical conductivity obtained in the present study is $2.6 \times 10^5$ S m$^{-1}$ for Mg$_2$Si: Sb0.5%Zn0.5% at room temperature (300 K). The electrical conductivity of double or multi-doped Mg$_2$Si is substantially larger when compared to the un-doped Mg$_2$Si ($15$ S m$^{-1}$). A small amount of dopants (0.5%~1.0%) is found to have a dramatic impact on the electrical conductivity. In all four multi-doped Mg$_2$Si samples, an increase of electrical conductivity were observed. The conductivities derived from infrared reflectivities show the correct trend expected from the free electron model. (i.e. the conductivity of Mg$_2$Si: Sb0.5%AI1.0% is higher than Mg$_2$Si: Sb0.5%Zn0.5%) as AI donates more electrons than Zn when substituted the Mg sites. The reverse was apparently observed in the bulk measurements. (Fig. 8) This discrepancy may be attributed to non-homogeneity of the dopants. Moreover, the free electron model is only a simplification and the true conductivity also depends on the effective mass of the conducting electron, which is related to the dispersive of the occupied conduction band. If the bulk measurements are more representative of the property of the sample, we may speculate that the effective mass of the conducting electrons in Mg$_2$Si: Sb0.5%Al1.0% is heavier. In fact, as shown in Table III, the derived effective mass of the electron in Mg$_2$Si: Sb0.5%Al1.0% of 0.346m$_e$ is heavier than Mg$_2$Si: Sb0.5%Zn0.5% of 0.316m$_e$. It is interesting to note that there is a distinctive discontinuity in the Mg$_2$Si: Sb0.5%Al0.5%Zn0.5% at 450K~500 which will be discussed below (vide supra).

From the temperature dependence of the electrical conductivity, the activation energy of the doped Mg$_2$Si samples in the temperature range, 300 K-800 K, can be defined from the Arrhenius equation $\rho = \rho_0 \exp(-E_t/kT)$, where $\rho$ is the electrical resistivity, $\rho_0$ is the high temperature resistivity, $E_t$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is the temperature. The value of $E_t$ can be determined from the plot of ln($\rho$) vs. (1/T). As shown in Fig. 8 (a1)&(a2), between 450 K and 550 K, the trend of Mg$_2$Si: Sb0.5%Al0.5%Zn0.5% does not
follow the relationship with increasing the temperature as the others. The sudden change of activation energy ($E_a$) further implies that a possible structure change has occurred.\textsuperscript{10} Since the high temperature crystal structure is still unknown, a definitive will characterization require a high temperature X-ray diffraction powder diffraction study.

Throughout the temperature range studied, the Seebeck coefficients ($S$) of Sb, Al, Zn multi-doped Mg$_2$Si samples are negative confirming they are n-type semiconductors, in agreement with the Hall coefficients. The values for the temperature dependent Seebeck coefficient ($S$) are quite similar for all doped samples, suggesting the dopants play a similar role to enhance the Seebeck coefficient. The Seebeck coefficient increased from -90 $\mu$V/K to -190 $\mu$V/K with increasing temperature and reached a maximum value at 900 K. The Seebeck coefficients for the doped Mg$_2$Si samples are comparable with the previously reported Bi, Pb, and Sb double-doped Mg$_2$Si.\textsuperscript{19} For un-doped Mg$_2$Si sample, the Seebeck coefficient increased initially with increasing temperature and reach the maximum value at 450 K. Above 450 K, the value of Seebeck coefficient started to decrease.

Fig. 8 (c) shows the calculated power factor ($S^2\sigma$) of doped Mg$_2$Si samples. The general trend of the calculated temperature dependent power factor increased initially and peaked at $\sim$750 K then drop with further increase of the temperature. The maximum power factor is due to the effect that Seebeck coefficient ($S$) increases faster than decrease in the electrical conductivity ($\sigma$). At further increase in temperature, the power factor decreases gradually, as the electrical conductivity ($\sigma$) becomes more important to power factor than the Seebeck coefficient ($S$). A peak power factor of 2.9 x 10$^{-3}$ W m$^{-1}$K$^{-2}$ was found at 500 K in Mg$_2$Si: Sb0.5%Al0.5%Zn0.5%, close to the possible structural phase transition. Fig. 8 (d1) shows the temperature dependent thermal conductivity of the doped Mg$_2$Si samples. The general trend of the thermal conductivities is to decrease with increasing temperature. This is obviously due to increase in phonon scatterings at higher temperature. At 310 K, the thermal conductivity of Mg$_2$Si: Sb0.5%Al0.5%Zn0.5% (5.6 W m$^{-1}$K$^{-1}$) is higher than other doped Mg$_2$Si samples. However, all the thermal conductivities of doped Mg$_2$Si samples are lower than un-doped Mg$_2$Si (6.2 W m$^{-1}$K$^{-1}$). Phonon scatterings become more efficient at the presence of heavier dopants in the lattice. Total thermal conductivities ($k_{total}$) can be separated into two contributions the lattice ($k_{ph}$) and the electronic ($k_{el}$) conductivity. The electronic conductivity ($k_{el}$) can be estimated by the Wiedemann-Franz law, where $k_{el}=\text{LoT}$ (the Lorentz number ($L$) is $2.45\times10^8 \text{ V}^2\text{K}^{-2}$).\textsuperscript{41} The lattice thermal conductivity ($k_{ph}$) can then be estimated by subtracting the electronic thermal conductivity ($k_{el}$) from the total thermal conductivity ($k_{total}$). Considering the major contribution of lattice thermal conductivity ($k_{ph}$) to the total thermal conductivity ($k_{total}$), Fig. 8 (d2) shows the temperature dependent of the lattice thermal conductivity ($k_{ph}$). Compared to Al, the heavier Zn dopants are better phonon scatters, leading to lower lattice thermal conductivity. The observed trend,Mg$_2$Si:Sb0.5%Al0.5%Zn0.5%>Mg$_2$Si:Sb0.5%Al1.0%>Mg$_2$Si:Sb0.5%Zn1.0%>Mg$_2$Si:Sb0.5%Al0.5%Zn0.5%>Mg$_2$Si:Sb0.5%Zn0.5%>Mg$_2$Si:Sb0.5%Zn1.0% is expected. Similarly, the lattice thermal conductivity of Mg$_2$Si: Sb0.5%Zn0.5% and Mg$_2$Si: Sb0.5%Zn0.5% samples are lower than others because the phonon scatterings become more efficient at the present of heavier Zn dopants. The only exception is Mg$_2$Si: Sb0.5%Al0.5%Zn0.5% which has a higher thermal conductivity than Mg$_2$Si: Sb0.5%Al1.0%. At this moment, we cannot provide a satisfactory explanation for this observation. Using the information obtained above, the temperature dependent figure of merits (ZT) were calculated. (Fig. 8 (e)) For each doped-Mg$_2$Si sample, ZT increased significantly with increasing temperature. A maximum ZT of 0.964 is found in Sb0.5%Zn0.5% doped Mg$_2$Si at 880 K.

**Conclusions**

The structural information of Sb Al Zn multi-doped Mg$_2$Si powder samples synthesized from spark plasma sintering have been investigated by angle dispersive synchrotron radiation X-ray diffraction, infrared reflectivity, electrical and thermal conductivity measurements. The small concentration of dopant (0.5%~1.0%) did not alter the cubic crystal structure of the host Mg$_2$Si, but expanded the crystal lattice noticeably. The electrical transport properties were characterized by mid-IR reflectivity and quasi-four probe measurements. Infrared reflectivity shows doped semiconductor character for all the samples at room temperature. The dc conductivities calculated from the analysis of the infrared reflectivity spectra employing the Drude-Lorentz model are in qualitative agreement with the conventional bulk four-probe measurements although the absolute values obtained from IR reflectivities are consistently lower. The electron concentrations ($N$) were determined from the Hall coefficients and plasma frequencies ($\omega_n$) of the infrared reflectivities. The multi-doped Mg$_2$Si are within the order 10$^{20}$ cm$^{-3}$, suggesting that all doped-Mg$_2$Si are doped semiconductors. The effective masses ranged from 0.255$m_0$ to 0.361$m_0$ showing different dopants have slightly effect on the band structure of Mg$_2$Si. A maximum thermoelectric figure of merit (ZT) of 0.964 was achieved in Sb0.5%Zn0.5% doped Mg$_2$Si sample at 880 K. The present study provides new results and insight on thermoelectric and electrical transport properties of Sb Al Zn multi-doped Mg$_2$Si from 300 K to 900 K. The information presented here may help to further enhance the performance of Mg$_2$Si-based thermoelectric materials.

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Notes and references
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A maximum ZT of 0.964 was found in Sb0.5%Zn0.5% doped Mg$_2$Si, which is comparable to the PbTe based thermoelectric materials.