Impact of Cr content on the thermoelectric properties of the Cr/Sb co-doped Mg2.2-xCrx(Si0.3Sn0.7)0.98Sb0.02 compound

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Abstract
The n-type Cr/Sb co-doped Mg2.2-xCrx(Si0.3Sn0.7)0.98Sb0.02 (0.0025 ≤ x ≤ 0.01) compounds were successfully fabricated by applying the solid state reaction-spark plasma sintering (SPS) technique. The impact of the active Cr content on the thermoelectric properties of the co-doped compound was systematically studied. Insights from the x-ray diffraction (XRD) results indicate the existence of single-phase material of the prepared compounds. Interestingly, the lattice constant and the electrical conductivity of the samples increases with the decrease of the Seebeck coefficient as the Cr content is becomes bigger. All the fabricated compounds could achieve an excellent power factor (PF) of 3.8–4.9 mWm⁻¹K⁻² in the range of 300–800 K. The lattice thermal conductivity declines with the increasing Cr amount. More specifically, the lowest κL of about 0.5 Wm⁻¹K⁻¹ was obtained while x = 0.01 at 650 K. The figure of merit (ZT) is also reduced by increasing the Cr content. A high ZT value of 1.4 was obtained while x = 0.0025 at 700 K.

1. Introduction
Magnesium compounds MgX (X = Si, Ge, Sn) and their respective solid solutions are considered economical and friendly candidates for the development of high-performance thermoelectric materials. The thermoelectric performance is commonly evaluated through the utilization of the figure of Merit (ZT), ZT = S²σT/κ, where S is the Seebeck coefficient, σ stands for the electrical conductivity, κ represents the thermal conductivity and T denotes the absolute temperature. Under this direction, a low lattice thermal conductivity and high carrier mobility are preferred for enhancing the figure of merit. Many studies in the literature have reported that the Mg₂Si₁₋ₓSnₓ-based solid solutions with a Si/Sn ratio near 0.3/0.7 exhibit the desired thermoelectric performance. This effect stems from the precipitated Sn-rich nano-phase with a very low lattice thermal conductivity value and the enhanced power factor (PF = S²σ) by the convergence of the heavy and light conduction bands [1, 2]. More attempts are conducted for controlling the semiconducting properties [3, 4] by doping additives into Mg₂X, e.g. p-type by doping with Ag and Cu, as well as n-type by doping with Sb, Al, and Bi. Especially, Sb has been reported to act as a donor and the most stable dopant in Mg₂Si. The effectiveness of the Sb doping could be close to 100% at low doping amounts [5, 6]. Tani et al reported that the electron concentration of Sb-doped Mg₅Si (Mg₅Si:Sb = 1:x) at 300 K could be increased from 2.2 × 10⁹ cm⁻³ to 1.5 × 10¹⁰ cm⁻³ while the x elevated from 0.001 to 0.02 [7]. In another interesting work, Gao et al [8] reported that the Mg₅Sio.7Sn0.3, doped with 5500 ppm of Sb can achieve ZT values as high as 0.54 at 650 K, while the band gap of Mg₅Si0.7Sn0.3 remained almost unchanged. It has been also been reported that small amounts of Sb in Mg₅Si would promote the precipitate formation, leading thus to a decrease in the thermal conductivity [9].

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As a substitution of Mn in MnSi$_2$, doping with Cr is anticipated to improve the thermoelectric properties [10, 11]. On top of that, a small amount of Cr has been found to enhance the electrical conductivity by increasing the hole concentration and decreasing the Seebeck coefficient [10]. Similar to Mn, Cr could also act as a substitution of Mg in Mg$_2$X. Many studies denote that the doped Cr could promote the formation of nano-precipitates, resulting in the reduction of the lattice thermal conductivity ($\kappa_L$) [12, 13]. The Co-doped Cr and Bi could result in a $\sim$15% reduction in the lattice thermal conductivity ($\kappa_L$) compared to the only Bi doped sample while retaining similar PF values [13]. Along these lines, in this work, Cr/Sb is co-doped into Mg$_2$Si$_{0.3}$Sn$_{0.7}$. The influence of the Cr content on the thermoelectric properties of the solutions was thoroughly investigated.

2. Experiment

2.1. Synthesis
High purity Mg (99.99%), Si (99.99%), Sn (99.99%), Sb (99.99%) and Cr (99.99%) powders were used to prepare a series of Mg$_{2.20-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ ($0.0025 \leq x \leq 0.01$) solid solutions by enforcing a two-step solid state reaction method. In addition, 10% excess Mg was taken to compensate for the loss of Mg [1] and the Sb content was predetermined as 0.02 [7]. The precursor elements were firstly weighted as per the stoichiometry, and dry-pressed into cylinders at 8 MPa after performing homogeneous mixing. Thereafter, the mixture was placed in an atmosphere furnace for the following two-step solid state reaction under argon atmosphere. The first and second synthesis reactions were performed at 923 K for 24 h and 973 K for 24 h, respectively. The final sintering of the compound was done at 923 K for 10 min at 6 MPa pressure in a graphite die under 0.5 atm Ar atmosphere by applying the spark plasma sintering (SPS) method. Then the sintered pellets were cut to an appropriate size for the subsequent measurements with a diamond wire cutter. The synthesis equipment is illustrated in figure 1.

2.2. Characterization
The phase purity and the crystal structure of the samples were analyzed carrying out x-ray diffraction (PANalytical Empyrean) measurements by using Cu Kα radiation (40 kV, 300 mA). The temperature dependent Seebeck coefficient ($S$) and the electrical conductivity ($\sigma$) were measured by the standard four-probe method by using an Ulvac-Rico ZEM-3 system under a helium atmosphere. The thermal conductivity ($\kappa$) of the pellets was calculated according to the following equation: $\kappa = \lambda C_p \rho$, where ‘$\lambda$’ is the thermal diffusivity, ‘$C_p$’ represents the specific heat and ‘$\rho$’ is density. The $\lambda$ lies in the range of 300–800 K, while it was measured on a Netzsch LFA-457 apparatus. In addition, the specific heat ($C_p$) was measured by performing differential scanning calorimetry (DSC Q20, TA Instruments) measurements. The density was determined by Archimedes’ method. Error in measurement of thermal conductivity is close to 8%. The microstructure of the fractured morphology was investigated by employing a scanning electron microscope (SEM, JEOL 6304F).
3. Results and discussion

The acquired XRD patterns of the Mg$_{2.20-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ compound are shown in figure 2(a). All the detected diffraction peaks confirm the existence of the patterns related to the Mg$_{2.0}$Si$_{0.3}$Sn$_{0.7}$ based solid solutions according to JCPDS #01-089-4254. As a result, the formation of a single phase is indicated.

As the Cr content increases, the 2$\theta$ of 69$^\circ$ moves towards the left, indicating that the lattice constant is growing due to the substitution by Cr, which has a larger ionic radius than Mg, as is depicted in figure 2(b). The lattice constants of the Mg$_{2.20-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ compound were calculated via the Rietveld refinement method and the results are illustrated in figure 2(c).

Figure 3 depicts the typical fracture morphology of the Mg$_{2.20-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ compound, where micro holes could be hardly observed in the matrix. The average grain size is estimated at about 2–10 $\mu$m. With larger magnification in figure 3(b), river pattern characteristics could be noticed, denoting the brittle rupture of the compound.

The temperature dependence of the electrical conductivity ($\sigma$) of the Mg$_{2.20-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ compound is depicted in figure 4(a). Interestingly, the electrical conductivity is enhanced significantly due to Cr doping, where the Cr$^{3+}$ substitution in the Mg$^{2+}$ site is expected to act as a donor [13]. The highest room temperature conductivity value of about 29 $\times$ 10$^4$ Sm$^{-1}$ was obtained with the compound Mg$_{2.19}$Cr$_{0.01}$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$. The electrical conductivity of the doped compounds decreases with the temperature, suggesting the manifestation of degenerate semiconductors with relatively high carrier concentration. Moreover, small differences in the electrical conductivity at employed different Cr content are recorded as the temperature becomes bigger.

Figure 4(b) displays the Seebeck coefficient ($\alpha$) for all Mg$_{2.20-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{0.98}$Sb$_{0.02}$ samples in the entire temperature range from 300 to 800 K. The negative value of $\alpha$ indicates the n-type conduction of all samples. The absolute value of the Seebeck coefficient displays an increasing trend with the rising temperature due to the increase in the carrier concentration by the intrinsic conduction. As the Cr content increases, the absolute value of the Seebeck coefficient decreases. The highest Seebeck coefficient of $\sim$220 mV K$^{-1}$ was obtained at about 800 K.
when the Cr content was 0.0025. Commonly, the Seebeck coefficient and the carrier concentration should satisfy the following equation, assuming the carrier mean-free path is independent of the energy

\[
\alpha = \frac{8\pi^2k_B^2T^{2/3}}{3eh^2}\left(\frac{\pi}{3n}\right)^{2/3}
\]

Here, \(k_B, e, h, m^*\) and \(n\) represent the Boltzmann constant, the charge of an electron, Planck’s constant, the carrier effective mass and the carrier density, respectively. The decrease of \(\alpha\) while increasing the Cr content may also indicate that an increase in the carrier concentration is the predominant mechanism over the electron–phonon scattering.

Figure 4(c) displays the extracted temperature-dependent power factor (PF) of the samples in the range of 300–800 K. The PF firstly increases and then decreases with the rising of the temperature. At room temperature, it could be noticed that the PF of the Mg₂₂₀₋ₓCrₓ(Si₀.₃Sn₀.₇)₀.₉₈Sb₀.₀₂ compound increases as the Cr content becomes bigger. However, at the temperature of about 800 K, the PF of the samples dramatically decreases while rising the Cr content. All the samples could achieve an excellent PF value of 3.8–4.9 mWm⁻¹K⁻² in the range of 300–800K. The highest PF of about 4.9 mWm⁻¹K⁻² appears when the Cr content is 0.0025 at 650 K. We have to underline that this PF value is larger than that of the reported in the literature Mg₂(Si₀.₄Sn₀.₆)₀.₀₇Bi₀.₀₃ (about 4 mWm⁻¹K⁻²) [1], Sb doped Mg₂Si (3 mWm⁻¹K⁻²) [16].

Figure 5(a) depicts the temperature dependence of the total thermal conductivity \(\kappa\) of the samples. All the \(\kappa\) value of the samples decrease with increasing the temperature at 300–650 K, whereas a slightly upward trend above 650 K is detected, which is mainly attributed to the bipolar diffusion that occurs in higher temperatures. Additionally, at low temperatures, \(\kappa\) depends strongly on \(x\) and becomes bigger by increasing \(x\) with the following condition: \(x \leq 0.0075\). However, the \(\kappa\) value at \(x = 0.01\) is nearly the same as that at \(x = 0.0075\), indicating that the influence of the Cr content on the total thermal conductivity is negligible while it exceeds 0.0075.

The lattice thermal conductivity \(\kappa_L\) could be calculated by using the following equation:

\[
\kappa_L = \kappa - \kappa_e
\]

where \(\kappa_e\) is the electronic thermal conductivity. \(\kappa_e\) can be calculated on the basis of the Wiedeman-Franz law by using the Lorentz number \(L\) [1, 17] and the electrical conductivity \(\sigma\) as follows:

\[
\kappa_e = LT\sigma
\]
Figure 5(b) shows the temperature dependence of the $\kappa_L$ in the thermal conductivity of the compounds. The $\kappa_L$ firstly declines while increasing the temperature but then an upward trend near 650 K is recorded. This effect could be ascribed to the weaker impact of scattering phonons in higher temperatures [18]. Additionally, the $\kappa_L$ declines with increasing the Cr amount. The lowest $\kappa_L$ of $\sim 0.5$ W m$^{-1}$K$^{-1}$ was obtained in the Mg$_{2.19}$Cr$_{0.01}$Si$_{0.7}$Ge$_{0.3}$ compound at 650 K. The reduction of $\kappa_L$ while doping Cr has been noticed in many studies [13]. Under this perspective, the reduction in $\kappa_L$ in solid solutions is commonly attributed to the mass disorder by promoting the phonon scattering. Also, it has been reported that the softening of the acoustic branches in the solid solutions could enhance the reduction of $\kappa_L$ [19]. Moreover, Cr is reported to have a tendency to form clusters inside the lattice [12] and hence CrSn$_2$-based nano-precipitates could be produced in the matrix [13], which may further enhance the scattering of the phonons and reduce $\kappa_L$ [20, 21].

The TE figure of merit (ZT) was also calculated for the different compounds and is depicted in figure 5(c). All compounds have similar ZT values at room temperature, but a temperature dependency at higher temperatures was detected. When the temperature reaches the value of about 700 K, the doped samples have the highest ZT values. More specifically, the $x = 0.0025$ compound has the highest ZT value of 1.4 at 700 K. This value is smaller than that of reported Cr/Al co-doped Mg$_3$(Si$_{0.5}$Sn$_{0.2}$) compound [13], but larger than that of the Cr/Sb co-doped Mg$_3$Si$_{0.75}$Sn$_{0.25}$ configuration [22]. It could be observed that the ZT values decreases with the increase of the Cr content. However, this reduction mitigates at a high Cr content, where the ZT value at $x = 0.0075$ is nearly the same as that at $x = 0.01$. The primary reduced ZT by increasing the Cr content is attributed to the reduced Seebeck coefficient and the increased thermal conductivity value.

Compared to Mg$_3$Si, increasing tin concentration in Mg$_3$Si$_{1-x}$Sn$_x$ would yield a systematic energy gap which shrinks near the Fermi level and then slightly overlaps the valence and conduction bands near Fermi energy. As the substitution of Si, Sb behaves as an electron donor (n-type) and it would promote Fermi level moves to the conduction states [23]. On the other hand, the addition of Cr in place of Mg is reported to not affect the valence bands much, but cause various new states to arise near the conduction band edges [12]. This change is attributed to the lifting of degeneracy of low-lying conduction bands.

Commonly, the manifestation of a higher ZT (> 1) indicates the better efficiency of thermoelectric materials. In this work, the Sb was doped to substitute Si atoms. Since the atomic radii for Si, Sn, and Sb are 110 pm, 145 pm, and 145 pm, respectively, the doping of Sb would lead to a change in mass and considerable size difference between the Si and the Sn sites. Moreover, the entry of Sb atoms may penetrate into the lattice while its content is $> 7500$ ppm [8], inducing thus high point defects. Higher point defects would cause higher mass fluctuation scattering effects and strain field fluctuation scattering, leading hence to the decline of $\kappa_L$ [24, 25].

Similarly, Cr could replace the Mg site in the compound, causing a marked lattice expansion and distortion of the structure, which could lead to a strong strain field fluctuation. All these phenomena yield a sharp decrease in the lattice thermal conductivity [26], inducing a large ZT compared to the reported non-doped Mg–Si–Sn [8, 26].

### 4. Conclusion

The single phase compounds of the n-type Cr/Sb co-doped Mg$_{2.2-x}$Cr$_x$(Si$_{0.3}$Sn$_{0.7}$)$_{1-x}$Sb$_x$0.02 (0.0025 $\leq$ $x$ $\leq$ 0.01) have been successfully fabricated by enforcing the solid state reaction-spark plasma sintering (SPS). A high ZT value of 1.4 could be obtained for the co-doped compound. Furthermore, all the compounds could achieve an excellent power factor (PF) of 3.8–4.9 mWm$^{-1}$K$^{-2}$ in the range of 300–800K. By increasing the Cr content a significant increase of the lattice constant and the electrical conductivity is observed. However, both the absolute value of the Seebeck coefficient and the lattice thermal conductivity are reduced. At a high Cr content (>0.0075), the additional Cr has a slight influence on the total thermal conductivity and ZT. Our work reveals the significance of the Cr/Sb co-doping on influencing the thermoelectric performance of Magnesium-based compounds Mg$_3$X (X = Si, Ge, Sn), while the studied compound could be also used for thermoelectric device operations at elevated temperature values.

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Data availability statement

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

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