Modeling of thermal conductivity in high performing thermoelectric materials

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Abstract. The enhanced TE-performance in Mg₂Si-Mg₂Sn based pseudo-binaries is presented, which is attributed to low thermal conductivity. Sn-Si alloying, reduces the lattice thermal conductivity due to mass fluctuation. Furthermore, miscibility gap in the Sn-Si substitution causes the formation of composites, with Si-rich and Sn-rich phases, which span from mm to nm scale, and these nano-inclusions reduce further lattice thermal conductivity.

1. Introduction

The world’s demand for energy is increasing, along with environmental impact. In fact, the majority of the energy actually produced by man is lost, as waste heat. Only an average of about 1/3 of the energy produced by thermal and nuclear power plants, and similarly, only 30% of the energy produced in the internal combustion engine is converted to useful work [1]. If only a portion of the enormous amount of unused waste heat, generated by domestic heating, automotive exhaust, and industrial processes could be recovered, it would cause a tremendous benefit in energy demands. Thermoelectricity (TE) could be of great use in energy harvesting [2, 3].

The thermoelectric performance is ranked by the figure of merit $ZT (ZT = S^2σT/κ)$, where $S$ is the Seebeck coefficient, $σ$ the electrical conductivity, $κ$ the total thermal conductivity and $T$ the absolute temperature. A highly-performing TE material should have high $S$ and $σ$ and low $κ$.

Amongst the various promising materials used in the field of thermoelectrics, Mg₂Si-based compounds have attracted much attention during the last years due to their high $ZT$ in the mid-temperature range, combined to the fact that they are environmentally friendly and they contain widely abundant constituent elements, such as Mg, Sn and Si, with low cost and low density, thus meeting the requirements for large scale production [4]. Tani & Kido [5] presented a $ZT$ as high as 0.86 for Bi-doped Mg₂Si, which seems to be the best $ZT$ reported for the binary system so far. When alloying with Sn, the ternary system Mg₂SiₓSn₁₋ₓ presents even higher performance ($ZT$ up to 1.4), due to its lower thermal conductivity that mainly originates from the Si/Sn mass fluctuation in the lattice [6, 7].

In this work we explore thermal conductivity in Sb-doped Mg₂Si₀.₆Sn₀.₄, by modeling the various mechanisms that act cumulatively increasing the phonon scattering.
2. Experimental
Sb-doped Mg$_2$Si$_{0.6}$Sn$_{0.4}$–type materials were synthesized by high purity starting elements, as described in ref. 8. Materials were characterized by powder XRD (PXRD) and found as of pure phase, without any traces of un-reacted Mg, Si, Sn. All major peaks indicate the nominal composition; however they are asymmetric (Fig.1a), with a shoulder at higher $2\theta$. In fact, Mg$_2$Si$_{0.6}$Sn$_{0.4}$ is a composite material which consists of Si-rich & Sn-rich phases in a matrix phase, as has been observed in other members of the same family [7, 9], formed due to the miscibility gap, and span from mm-range down to nm-range [9], as shown in Fig.1b. PXRD diagrams were taken by a Rigaku SmartLab System, while TEM observations were carried out using a JEOL 120CX microscope operating at 100 kV. Thermal conductivity was measured using a laser flash technique on a NETZSCH LFA-457 apparatus, as described in ref. 8. The electrical conductivity and the Seebeck coefficient were determined simultaneously using an ULVAC ZEM-3 (Sinku-Riko) instrument.

![PXRD pattern for Sb-doped Mg$_2$Si$_{0.6}$Sn$_{0.4}$ and TEM micrograph with several nano-scale inclusions](image)

*Figure 1* (a) PXRD pattern for Sb-doped Mg$_2$Si$_{0.6}$Sn$_{0.4}$. In the inset is shown the observed asymmetry of the (220) peak. (b) Dark field TEM micrograph with several nano-scale inclusions (white spots).

3. Results and discussion
Thermal conductivity consists of two additive parts ($\kappa = \kappa_L + \kappa_E$), the lattice ($\kappa_L$) and the electronic ($\kappa_E$) contribution. The electronic contribution to thermal conductivity is given by $\kappa_E = L \sigma T$, where $L$ is the Lorenz number and $\sigma$ the electrical conductivity. The Lorenz number ($L$) was determined from Seebeck coefficient measurements ($S$), through the reduced Fermi level ($\eta = E_F/k_BT$) assuming acoustic phonon scattering:

$$L = \left(\frac{k_B}{e}\right)^2 \left[ \frac{3F_0(\eta)F_2(\eta)-4F_1^2(\eta)}{F_0(\eta)} \right], \quad S = \frac{k_B}{e} \left[ \frac{2F_0(\eta)}{F_0(\eta)-\eta} \right]$$

where $F_j(\eta)$ is the Fermi integral. The resulting lattice thermal conductivity is presented as experimental points in Figure 2a.

3.1. Modeling lattice thermal conductivity
To understand the mechanisms of phonon scattering, semi-classical theoretical calculation based on the modified Callaway’s model [10] is conducted:

$$\kappa_L(T) = \frac{k_B}{2\pi^2u} \left(\frac{k_B}{\hbar}\right)^3 \tau_{0,\eta}^{\eta/\tau} \tau_c(x) \frac{x^4e^x}{(e^x-1)} dx$$

(2)
where $k_B$ is the Boltzmann’s constant, $\hbar$ is the Plank constant, $T$ is the absolute temperature, $\theta_D$ the Debye temperature, $x=\hbar\omega/k_BT$, and $\tau_\phi$ is the phonon relaxation time, which, in our model, combines the scattering from Umklapp/Normal processes ($\tau_{UN}$), nano-structured precipitates ($\tau_{NP}$), alloying ($\tau_A$) and grain boundaries ($\tau_B$) by the equation [11, 12]

$$\frac{1}{\tau_c(T,\omega)} = \frac{1}{\tau_B} + \frac{1}{\tau_{NP}(\omega)} + \frac{1}{\tau_A(\omega)} + \frac{1}{\tau_{UN}(T,\omega)}$$

Some of the mechanisms depend only on geometrical features ($\tau_B$), other on phonon frequency ($\omega$) while Umklapp on both temperature and phonon frequency.

Phonon scattering due to interfaces and grain boundaries ($\tau_B$) is given by [13]:

$$\tau_B^{-1} = \frac{4}{3} \frac{L}{t} \quad \text{or} \quad \tau_B^{-1} = \frac{u}{L_{eff}} \quad \text{where} \quad L_{eff} = \frac{3}{4} \frac{t}{1-t}$$

where $t$ is the phonon transmissivity and $L$ is the average grain size, or scaled to $L_{eff}$.

When alloying, the solute atom scattering is accounted by the effective medium approach using a Rayleigh-like expression as described by Klemens [14]:

$$\tau_x^{-1}(\omega) = A\omega^4 \quad , \quad A = \frac{\delta^3}{4\pi^2} \left[ x(1-x) \left( \frac{\Delta M}{M} \right)^2 + e \left( \frac{\Delta\delta}{\delta} \right)^2 \right]$$

where $\delta$ is the radius of the solute atom, $M$ is the molar host weight, $\Delta M/M$ is the mass fluctuation, $\Delta\delta/\delta$ is the strain field fluctuation and $\epsilon$ an adjustable parameter.

The Umklapp scattering, derived from 2nd order perturbation is usually given by [15]:

$$\tau_U^{-1}(\omega,T) = B\omega^2T \exp \left( -\frac{T_\phi}{3T} \right) \quad , \quad B = \frac{\hbar \gamma^2}{Mu^2T_\phi}$$

where $\gamma$ is the Gruneisen parameter and $M$ the average mass. For normal phonon–phonon scattering, several models were proposed [16], however, it is generally accepted that $(\tau_N)^{-1} = \beta(\tau_U)^{-1}$, where $\beta$ is the ratio of two process scattering and is assumed to be temperature independent [12]. Therefore we treat both mechanisms by the same expression, as $\tau_{UN} = \tau_U/(\beta+1)$. The value of parameter $\beta$ is determined by fitting experimental data of pure Mg$_2$Si$_{0.6}$Sn$_{0.4}$.

### 3.2. The effect of nano in thermal conductivity

Relaxation time of phonon scattering due to the nano-scale inclusions is given by a Mathiessen-type combination of short-wavelength and long-wavelength scattering [17]:

$$\tau_N^{-1}(\omega) = u(\sigma_S^2 + \sigma_L^2)^{-1} v_N$$

$$\sigma_s = 2\pi R^2 \quad , \quad \sigma_L(\omega) = \frac{4\pi R^2}{9} \left( \frac{\Delta\rho}{\rho} \right)^2 \left( \frac{\omega R}{u} \right)^4$$

where $v_N$ is the density of the nano particles, $\sigma_s$ & $\sigma_L$ are the short wavelength (geometrical) and long wavelength (Rayleigh-type) scattering cross section (geometrical), $R$ is the average particle radius, $\rho$ is the medium density and $\Delta\rho$ is the density difference between the particle and matrix materials.

Figure 2 shows the effect of nano-structuring in thermal conductivity. At low temperatures, thermal conductivity is increasing, due to the increasing nature of the integral in eq. 2, reaches a maximum, and then decays to a $1/T$ law due to Umklapp scattering. Standard material properties, like density, Debye temperature, speed of sound, Gruneisen parameter, etc, were taken by linear interpolation.
between the corresponding values of the two end member materials (Mg$_2$Si & Mg$_2$Sn), received from literature [18]. Material characteristics like the average grain size (L=2μm) and average size of nanoparticles (2R=22nm) were taken from SEM and TEM measurements [8, 9]. The nano-particle density was roughly estimated by the dark field TEM image and was further refined by adjusting it as the theoretical curve fits the experimental data.

![Figure 2](image1.png)

**Figure 2** (a) Calculated lattice thermal conductivity (lines) and experimental points. (b) Phonon mean free path as a function of the phonon frequency, along with the various phonon scattering mechanisms. 

Fig.2a shows the effect of nano: Based on the above described model, the top solid curve is without encountering nano, the middle one with nano and the lower (dashed) with 10X density of nano particles. Depending of the nano density, the characteristic peak in lattice thermal conductivity is less and less profound; while the relaxing part (after the peak) considerably deviates from the 1/T law. Clearly, the experimental points are below the top curve (without nano) indicating that an additional phonon scattering mechanism is required, and is better described by the middle curve (with nano).

Fig.2b shows the phonon mean free path (MFP) at 500K, as a function of phonon frequency ($\omega/\omega_D$). The various acting mechanisms that are reducing the lattice thermal conductivity are shown in figure caption. At low frequencies, phonon MFP is limited by the grain boundary (GB) scattering, while at high frequencies by a combination alloying & Umklapp processes. In the absence of nano, the total phonon MFP is smoothly changing from the GB scattering to alloy/Umklapp scattering as shown by the orange curve. However, when nano is encountered (green curve), a considerable amount of mid-range phonons are scattered by nano inclusions (solid black curve). When nano density is increased by X10, the “nano-curve” (dotted green line) considerably filters out a much larger portion of mid-range phonons, resulting in a significantly lower lattice thermal conductivity.

4. Summary
In this work we model thermal conductivity in Sb-doped Mg$_2$Si$_{0.6}$Sn$_{0.4}$, a high performing thermoelectric material. Several mechanisms have been encountered that act cumulatively limiting the phonon mean free path. Standard material properties, were taken by linear interpolation between the corresponding values of the two end member materials (Mg$_2$Si & Mg$_2$Sn), received from literature. Analysis has shown that lattice contribution to thermal conductivity can be effectively modeled only if nano-inclusions are taken into account. These nano-inclusions are Si-rich and Sn-rich phases which span from mm to nm scale and reduce further lattice thermal conductivity.
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