Improvement of Thermoelectric Properties through Reduction of Thermal Conductivity by Nanoparticle Addition and Stoichiometric Change to Mg$_2$Si

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Motivation

Estimated U.S. Energy Use in 2013: ~97.4 Quads

Source: LLNL, 2014. Data is based on DOE/EIA-0335(2014-03), March 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in EIA-equivalent values by assuming a typical fossil fuel plant heat rate. The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 60% for the residential and commercial sectors 80% for the industrial sector, and 23% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-416027

https://flowcharts.llnl.gov/archive.html
Motivation

https://www.alphabetenergy.com/how-thermoelectrics-work/
Motivation

Figure of Merit ($ZT$) is a measure of the thermoelectric material’s efficiency in converting thermal energy to electrical current. It is defined by the following equation:

$$ZT = S^2 \frac{\sigma T}{k}$$

Rull-Bravo, RSC Advances, 2015
Motivation

Why Use Mg\(_2\)Si?

- Mg is earth abundant in Utah and much of the US
- Mg\(_2\)Si is a relatively simple compound when compared to the other thermoelectrics
- Mg is inexpensive, resulting in the production of Mg\(_2\)Si being less expensive

https://mrdata.usgs.gov/geochem/doc/averages/mg/usa.html
Methodology

Molecular Dynamics

(Large-scale Atomic/Molecular Massively Parallel Simulator)

\[ ZT = S^2 \frac{\sigma T}{k} \]

\[ k = k_p + k_e \]

LAMMPS can only calculate \( k_p \), which makes the follow up of experimental research to measure \( ZT \) critical.

http://lammps.sandia.gov/#nogo
Experimental Setup

- Periodic Boundaries
- Extended modified embedded atom method (MEAM) potential

Zhang, Hengji, CMS, 2015
Experimental Setup

- Pure $\text{Mg}_2\text{Si}$
- Pure $\text{Mg}_2\text{Si}$ with Si NP
- $\text{Mg}_x\text{Si}_y$ with 41.37% Si (matching the Si % of the sample with 8 Si NPs)
## Experimental Setup

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>300 K (Wm(^{-1})K(^{-1}))</th>
<th>600 K (Wm(^{-1})K(^{-1}))</th>
<th>900 K (Wm(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg(_2)Si</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
<tr>
<td>Mg(_2)Si with 1 Si NP</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
<tr>
<td>Mg(_2)Si with 2 Si NP</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
<tr>
<td>Mg(_2)Si with 4 Si NP</td>
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<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
<tr>
<td>Mg(_2)Si with 8 Si NP</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
<tr>
<td>Mg(_2)Si with 16 Si NP</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
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<td>Mg(_x)Si(_x) 34.29 % Si (matching stoichiometry of Mg(_2)Si with 1 Si NP)</td>
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<td>Mg(_x)Si(_x) 49.55 % Si (matching stoichiometry of Mg(_2)Si with 16 Si NP)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
<td>(k_p = ?)</td>
</tr>
</tbody>
</table>
Methodology

- Nonequilibrium Molecular Dynamics (NEMD)
- Applied Heat Flux
- Total simulated time of 15 ns
Methodology

Fourier's Law

\[ q = -k \frac{\Delta T}{\Delta x} \quad \Rightarrow \quad k = -q \frac{\Delta x}{\Delta T} \]
Uncertainty Calculations

• Simulations were run at the 3 different equilibration temperatures as previously described, except that no heat flux was applied (we assumed stoichiometry did not significantly affect the uncertainty in temperature)

• The temperatures for each chunk were then averaged all together
• The absolute value of the difference between this value and the target equilibration temperature was taken as our uncertainty in temperature

• This value was then added to and subtracted from the ΔT in Fourier’s Law to obtain the minimum and maximum $k_p$ values, and therefore their associated $k_p$ uncertainties

<table>
<thead>
<tr>
<th>Equilibration Temperature (K)</th>
<th>Uncertainty (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.774</td>
</tr>
<tr>
<td>600</td>
<td>0.721</td>
</tr>
<tr>
<td>900</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Effect of NP Placement on $k_p$

- Some simulations had Si NPs in the walls and heat source/sink
- To ensure that this wasn’t a problem, 2 simulations were run with 8 Si NPs each; one had an Si NP in the heat sink/wall area, the other did not.
- Their $k_p$ values were 2.876 (Wm$^{-1}$K$^{-1}$) and 3.063 (Wm$^{-1}$K$^{-1}$), respectively, resulting in a percent change in $k_p$ of 6.499%, which we considered negligible.
Results – Pure Mg$_2$Si

<table>
<thead>
<tr>
<th>Work</th>
<th>$k_p$ of Pure Mg$_2$Si at 300 K (Wm$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaBotz</td>
<td>7.8</td>
</tr>
<tr>
<td>This Work</td>
<td>8.454 ± 1.094</td>
</tr>
</tbody>
</table>

We determined that our calculated value for $k_p$ above was sufficiently close that of Labotz, such that we could begin simulation of off-stoichiometry samples of Mg$_2$Si and calculation of their respective values for $k_p$.

LaBotz, JES, 1963
Results – Mg$_2$Si with Si NPs

**FIGURE 3:** Lattice thermal conductivity ($k_p$) vs. number of Si NPs present in Mg$_2$Si samples at 300, 600, and 900 K. Included is an estimation of $k_p$ for the 300 K equilibration temperature case, using Eqn.[13], denoted by NP at 300 K Theor.
Results – Mg$_2$Si with Si NPs

**FIGURE 5:** Lattice thermal conductivity ($k_p$) vs. temperature ($T$) for pure Mg$_2$Si (0 NPs) and Mg$_2$Si samples with 1, 2, 4, 8, and 16 Si NPs.
One Si NP Case

- Unexpectedly, the 1 NP cases resulted in lower in $k_p$ values than their respective 2 NP cases
- We thought this might have to do with the NP spacing

- It appears that the closer the Si NP concentration is to the center of the sample, the lower the $k_p$, despite no change in stoichiometry
Results – Mg$_2$Si with Si Substitutionals

**FIGURE 4**: Lattice thermal conductivity ($k_p$) vs. percent Si present in Mg$_2$Si samples at 300, 600, and 900 K. The percent Si values correspond to the stoichiometry of the sample of pure Mg$_2$Si (33.33% Si), and respective samples of Mg$_2$Si having 1, 2, 4, 8, and 16 Si NPs.
Results – Mg$_2$Si with Si Substitutionals

**FIGURE 6:** Lattice thermal conductivity ($k_p$) vs. temperature ($T$) for Mg$_2$Si samples with dispersed Si atoms, respectively matching the stoichiometry of the Mg$_2$Si samples with 0, 1, 2, 4, 8, and 16 Si NPs.
Results – Table Summaries

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>300 K (Wm(^{-1})K(^{-1}))</th>
<th>600 K (Wm(^{-1})K(^{-1}))</th>
<th>900 K (Wm(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg(_2)Si</td>
<td>8.454 ±1.094</td>
<td>4.199 ±0.342</td>
<td>3.533 ±0.705</td>
</tr>
<tr>
<td>Mg(_2)Si with 1 Si NP</td>
<td>5.252 ±0.416</td>
<td>3.275 ±0.176</td>
<td>2.428 ±0.261</td>
</tr>
<tr>
<td>Mg(_2)Si with 2 Si NP</td>
<td>5.877 ±0.586</td>
<td>3.456 ±0.312</td>
<td>2.987 ±0.626</td>
</tr>
<tr>
<td>Mg(_2)Si with 4 Si NP</td>
<td>4.553 ±0.387</td>
<td>2.972 ±0.205</td>
<td>2.204 ±0.277</td>
</tr>
<tr>
<td>Mg(_2)Si with 8 Si NP</td>
<td>2.876 ±0.211</td>
<td>1.930 ±0.119</td>
<td>1.992 ±0.323</td>
</tr>
<tr>
<td>Mg(_2)Si with 16 Si NP</td>
<td>1.791 ±0.124</td>
<td>1.649 ±0.157</td>
<td>1.280 ±0.214</td>
</tr>
<tr>
<td>Mg(_x)Si(_x) 34.29 % Si (matching stoichiometry of Mg(_2)Si with 1 Si NP)</td>
<td>6.346 ±0.624</td>
<td>3.749 ±0.283</td>
<td>2.676 ±0.369</td>
</tr>
<tr>
<td>Mg(_x)Si(_x) 35.32 % Si (matching stoichiometry of Mg(_2)Si with 1 Si NP)</td>
<td>5.015 ±0.441</td>
<td>3.001 ±0.244</td>
<td>2.065 ±0.296</td>
</tr>
<tr>
<td>Mg(_x)Si(_x) 37.29 % Si (matching stoichiometry of Mg(_2)Si with 1 Si NP)</td>
<td>3.669 ±0.272</td>
<td>2.430 ±0.186</td>
<td>1.387 ±0.151</td>
</tr>
<tr>
<td>Mg(_x)Si(_x) 41.37 % Si (matching stoichiometry of Mg(_2)Si with 1 Si NP)</td>
<td>2.300 ±0.133</td>
<td>1.784 ±0.126</td>
<td>1.591 ±0.264</td>
</tr>
</tbody>
</table>
| Mg\(_x\)Si\(_x\) 49.55 % Si (matching stoichiometry of Mg\(_2\)Si with 1 Si NP) | 1.300 ±0.053                   | 1.064 ±0.117                   | 0.9347 ±0.292 }
Conclusions

- Increasing the atomic percent Si, either through substitutional atoms or Si NPs, decreases $k_p$
- Samples with substitutional Si atoms resulted in greater decreases in $k_p$ when compared to the $k_p$ of the samples with Si NPs
- Boundary resistance, rather than reduction in mean free path, seems have the greater influence in reducing $k_p$ in the samples with Si NPs for the 1 and 2 NP cases
Future Work

- Experimental research will need to verify that these nanostructures actually result in an increased $ZT$ for $\text{Mg}_x\text{Si}_x$ as LAMMPS cannot account for changes in $k_e$.
- Further work should be done to understand why substitutional Si atoms lower $k_p$ more than the stoichiometric equivalent of Si NPs in $\text{Mg}_2\text{Si}$.
- Further should be done to understand more fully how concentrations of stoichiometric changes at certain locations, such as Si NPs at the halfway point between a heat source and sink, can change $k_p$. 
References


Acknowledgements

1. The Utah Energy Research Triangle Program from the Governor's Office of Energy Development provided the funding for this project.
Questions?