Tailoring the lattice thermal conductivity of materials for thermoelectric applications

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Basic problem

How is energy (heat) transported in a semiconducting material due to the temperature gradient?

Fourier law: $J = -\kappa \nabla T$; $J$ - heat current, $\kappa$ - thermal conductivity
Outline

- Thermoelectric energy conversion for ICT applications
- Basic concepts related to lattice thermal conductivity
- Strategies to design the lattice thermal conductivity of:
  - Bulk crystalline materials
  - Bulk materials with atomic scale disorder
  - Nanostructured materials
- Summary and outlook
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Relevance for ICT-Energy

Thermoelectric energy conversion

transformation heat into electricity

Thermoelectric figure of merit:

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

- \( \sigma \): electrical conductivity
- \( S \): Seebeck coefficient
- \( T \): temperature

We need materials with low \( \kappa \)!
Thermoelectric energy conversion in ICT

Powering autonomous wireless sensor networks

Wireless sensors applications:

- smart cities
- smart environment
- smart water
- smart metering
- security
- retail
- logistics
- industrial control
- smart agriculture
- smart farming
- automation
- eHealth
Thermoelectric energy conversion in ICT

Active solid state cooling

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Heat is transported by vibrations of atoms around equilibrium positions (and also by electrons).

\[ ZT = \frac{\sigma S^2 T}{\kappa_{\text{elec}} + \kappa_{\text{latt}}} \Rightarrow \]

\( \kappa_{\text{latt}} \) can be tailored separately from electronic properties!
Lattice vibrations

This problem is analogous to that of coupled harmonic oscillators.

Single oscillator:

- Mass: $M$
- Restoring force: $F = -kx$
- Distance from equilibrium: $x$
- Spring constant: $k$
- Frequency: $\omega^2 = \frac{k}{M}$
- Energy: $U = \frac{1}{2} kx^2$
Lattice vibrations and concept of phonons

Atomic displacements from equilibrium:

\[ \tilde{u} \sim \exp(qx - \omega t) \cdot \tilde{e}_u \quad \text{phonon modes} \]

- \( \tilde{q} = \frac{2\pi}{\lambda} \cdot \tilde{e}_x \) - wave vector
- \( \lambda \) - wavelength
- \( \tilde{e}_x \) - propagation direction
- \( \tilde{e}_u = \tilde{e}_x \) - longitudinal
- \( \tilde{e}_u = \tilde{e}_y \) - transverse
- \( \tilde{e}_u = \tilde{e}_z \) - transverse

Phonon dispersion:

\[ \omega(q) = \sqrt{\frac{2k}{M} (1 - \cos(qa))} \]
Phonons in diatomic materials

Any physical property related to lattice vibrations can be described using the concept of phonon modes.

- Longitudinal acoustic (LA)
- Transverse acoustic (TA)
- Longitudinal optic (LO)
- Transverse optic (TO)

Graph showing frequency vs. momentum for Si with modes LA, LO, TO, and TA.
Phonon interactions with other phonons

Coupled anharmonic oscillators:

Single oscillator:

Phonon-phonon interaction

\[ U = \frac{1}{2} kx^2 + \frac{1}{6} k_3 x^3 + \ldots \]

Dominant in bulk crystalline materials
Scattering due to atomic scale defects and interfaces.


Dominant in alloys and nanostructures
Lattice thermal conductivity

\[ \kappa_{\text{latt}} = \sum_{\mathbf{q}, s} \hbar \omega_{\mathbf{q}, s} \frac{\partial n_{\mathbf{q}, s}}{\partial T} v_{\mathbf{q}, s}^2 \tau_{\mathbf{q}, s} \]

- \( \mathbf{q} \) - phonon wave vector; \( s \) - phonon mode (TA, LA, TO, LO)
- \( \omega_{\mathbf{q}, s} \) - phonon frequencies
- \( n_{\mathbf{q}, s} = \frac{1}{\exp (\hbar \omega_{\mathbf{q}, s}/k_B T) - 1} \) - phonon occupations
- \( v_{\mathbf{q}, s} = \frac{\partial \omega_{\mathbf{q}, s}}{\partial \mathbf{q}} \) - group velocities
- \( \tau_{\mathbf{q}, s} \) - phonon lifetimes due to phonon interactions

By manipulating \( \omega_{\mathbf{q}, s} \) and \( \tau_{\mathbf{q}, s} \), we can tailor their \( \kappa_{\text{latt}} \)!
Lattice thermal conductivity and acoustic phonons

- \( \kappa_{\text{latt}} = \sum_{\mathbf{q},s} \hbar \omega_{\mathbf{q},s} \frac{\partial n_{\mathbf{q},s}}{\partial T} v_{\mathbf{q},s}^2 \tau_{\mathbf{q},s} \)

- \( v_{\mathbf{q},s} = \frac{\partial \omega_{\mathbf{q},s}}{\partial \mathbf{q}} \) - group velocities

- \( v_{\mathbf{q},\text{LA/TA}} \gg v_{\mathbf{q},\text{LO/TO}} \)

- Heat is carried mainly by acoustic modes in most materials.

![Graph showing frequencies of different phonon modes](image-url)
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Low lattice thermal conductivity in bulk materials

Energy: \[ U \approx \frac{1}{2} kx^2 + \frac{1}{6} k_3 x^3 \]

Conventional guidelines from the analysis of acoustic modes only:

- Large number of atoms in the unit cell.
- High average atomic mass.
- Weak interatomic bonding (small \( k \)).
- High anharmonicity (large \( k_3 \)).

PbTe - partial exception to the conventional guidelines

- One of the best bulk thermoelectrics at \( \sim 700 \) K due to low \( \kappa_{\text{latt}} \).
- Used for waste heat recovery applications.

\[
\begin{array}{c|c}
\text{Temperature (°C)} & \text{Thermal conductivity (W/mK)} \\
\hline
G. J. Snyder and E. S. Toberer, \\
\text{Nature Mater. 7, 105 (2008)}
\end{array}
\]
PbTe - partial exception to the conventional guidelines

- High average atomic mass (Pb - 207.2, Te - 127.6).
- Unusually low $\kappa_{\text{latt}}$ for a material with a small unit cell (2 atoms):

<table>
<thead>
<tr>
<th>Material</th>
<th>Si</th>
<th>Ge</th>
<th>Bi</th>
<th>PbTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$ (W/mK) at 300 K</td>
<td>155</td>
<td>65</td>
<td>8</td>
<td>2</td>
</tr>
</tbody>
</table>
PbTe - partial exception to the conventional guidelines

Close to the phase transition to a rhombohedral structure:

Soft transverse optical (TO) modes:
PbTe - partial exception to the conventional guidelines

- Weak bonding and high anharmonicity for TO modes, but not for heat carrying acoustic modes!
- The main effect: soft TO modes interact strongly with acoustic modes.
- Low phonon lifetimes and lattice thermal conductivity.

Conventional guidelines do not provide the full picture!
Experimental evidence of strong acoustic-optical interaction in PbTe

Detailed information on phonon dynamics using new experimental techniques/instrumentation:

O. Delaire et al., Nature Mater. 10, 614 (2011)
Theoretical evidence of strong acoustic-optical interaction in PbTe

Detailed information on phonon dynamics using new quantitative theories:

Z. Tian et al., PRB 85, 184303 (2012)
First principles approach to calculate lattice thermal conductivity

$M$ $k, k_3$ need to be calculated

Energy: $U \approx \frac{1}{2} kx^2 + \frac{1}{6} k_3 x^3$

No fitting parameters, atomic structure is the only input!

Usually very good agreement with experiments.

D. A. Broido et al., APL 91, 231922 (2007)
Increasing acoustic-optical phonon interaction to reduce $\kappa_{\text{latt}}$ of PbTe

Drive PbTe closer to the phase transition e.g. via strain
$\Rightarrow$ softening of TO modes.

Tensile [001] strain: $\eta = (a_\parallel - a_0)/a_0 = +1.15\%$.
Increasing acoustic-optical phonon interaction to reduce $\kappa_{\text{latt}}$ of PbTe

- Phonon lifetimes are reduced at all frequencies.
- $\kappa_{\text{latt}}$ of strained PbTe is reduced by a factor of 1.5 compared to PbTe.

R. Murphy, É. Murray, S. Fahy, and I. Savić, submitted
Bi$_2$Te$_3$ - another efficient thermoelectric material

- The best bulk thermoelectric at $\sim 300$ K due to low $\kappa_{\text{latt}}$.
- Used for environmental heat harvesting and solid state cooling.

G. J. Snyder and E. S. Toberer, Nature Mater. 7, 105 (2008)
Bi$_2$Te$_3$ is structurally related to PbTe:

Very low $\kappa_{\text{latt}}$ can be explained by conventional guidelines:

- High average atomic mass
- Complex unit cell (5 atoms)
- Weak bonding
- High anharmonicity

Conventional design rules are very useful nevertheless.

Nature Comm. 5, 3525 (2014)

PRB 90, 134309 (2014)
SnSe - new record thermoelectric material

IV-VI compound like PbTe:

A factor of 2 – 3 lower $\kappa_{\text{latt}}$ than that of PbTe despite much lighter atoms.

Low $\kappa_{\text{latt}}$ values can be explained by other conventional rules:

- Complex unit cell (8 atoms)
- Weak bonding
- High anharmonicity

$ZT \sim 2.6$ at 900 K: the highest reported $ZT$ in any material!

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A few types of atomic scale defects in materials:

- **Substitutional impurity**
- **Vacancy**
- **Interstitial impurity**
Atomic scale defects scatter short-wavelength phonons.
Si$_x$Ge$_{1-x}$ alloys

- One of the best thermoelectrics at $\sim 900$ K due to fairly low $\kappa_{\text{latt}}$.
- Used for power generation in space missions.

G. J. Snyder and E. S. Toberer, Nature Mater. 7, 105 (2008)
Mass disorder strongly reduces the lattice thermal conductivity of SiGe alloys with respect to Si and Ge.

J. Garg et al., PRL 106, 045901 (2011)

Atomic mass: Si - 28.1, Ge - 72.6
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Nanostructured materials

A few types of interfaces:

Between different materials

Between different crystal orientations (grain boundaries):
Nanostructured materials

Interfaces scatter mid/long-wavelength phonons.
Proof-of-concept: thin film superlattices

Considerably reduced $\kappa_{\text{latt}}$ with respect to bulk due to interfaces

- Si/Ge superlattices grown by MBE.
  

- Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices grown by MOVPE.
  
  Nature **413**, 597 (2001)

- PbTe/PbSe quantum dot superlattices grown by MBE.
  
  Science **297**, 2229 (2002)
Bulk nanostructured materials

Self-formed nanoscale inclusions driven by phase segregation

Example: AgPb$_{18}$SbTe$_{20}$

$\kappa_{\text{latt}}$ is 4 – 5 times smaller than that of PbTe due to nanoparticles

Combine atomic scale defects with interfaces ⇒ scatter short- and mid/long-wavelength phonons simultaneously.
Nanoparticles embedded in alloys

ErAs nanoparticles in a InGaAs matrix lead to significantly reduced $\kappa_{\text{latt}}$ with respect to InGaAs.

APL 87, 112102 (2005); PRL 96, 045901 (2006)
Bulk nanocomposites

Assembly of nanosized particles by ball-milling and hot-pressing of alloys.

Very low $\kappa_{\text{latt}}$ due to interfaces and alloy disorder.

- (Bi,Sb)$_2$Te$_3$ alloys:
  Science 320, 634 (2008)

- SiGe alloys:
  Nano Lett. 8, 4670 (2008)
SiGe nanodots in a Si matrix

Another combination of nanostructuring and alloy disorder leads to very low $\kappa_{\text{latt}}$ values.

SiGe nanodots in a Si matrix

- Planar multilayers: interfaces scatter mid-to-low frequency phonons.
- Nanodot multilayers: nanodots scatter mid-to-low frequency phonons even more strongly.
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SiGe nanodots in a Si matrix

- Planar multilayers: interfaces scatter mid-to-low frequency phonons.
- Nanodot multilayers: nanodots scatter mid-to-low frequency phonons even more strongly.
Combining all the mechanisms that scatter different wavelength phonons:

PbTe with Na dopants, SrTe nanoparticles and grain boundaries.

$\kappa_{\text{latt}}$ is by a factor of $2 - 3$ lower than that of PbTe due to point defects, nanoparticles and grain boundaries.

Record ZT value at the time: $ZT \sim 2.2$ at 900 K.

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Thermoelectric materials are promising candidates for power generation and solid state cooling in ICT.

Low lattice thermal conductivity is required for efficient thermoelectric energy conversion.

New bulk materials with low lattice thermal conductivity are being discovered, guided by both conventional and unconventional design rules.

Introducing atomic scale crystal imperfections and interfaces usually leads to considerably lower lattice thermal conductivity than that of bulk materials.
To achieve efficient thermoelectric conversion, we need new strategies to simultaneously suppress lattice thermal conductivity and preserve electronic thermoelectric properties.

We need new experimental and theoretical methods, and more intense interaction among them, to understand the problem of coupled electrons and lattice vibrations.

We need not only more efficient, but also cheaper and environment-friendly thermoelectric materials.