Glass-like thermal conductivity in high efficiency thermoelectric materials

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Outline

\[ \kappa_L = \frac{1}{3} \int C \nu_g^2 \tau d\omega \]

\( \nu_g \) - phonon group velocity
\( \tau \) - phonon relaxation time

**Group velocity (\( \nu_g \))**
- Structural complexity
  - Yb\(_{14}\)MnSb\(_{11}\)
  - Ca\(_5\)Al\(_2\)Sb\(_6\)
  - Ca\(_3\)AlSb\(_3\)

**Scattering (\( \tau \))**
- Intrinsic point defects
  - La\(_{3-x}\)Te\(_4\)
  - Zn\(_4\)Sb\(_3\)
- Nanostructures
  - Zn\(_4\)Sb\(_3\)
  - PbTe
Designing low $\kappa_L$ materials - group velocity

\[ \kappa_L = \frac{1}{3} \int C v_g^2 \tau d\omega \]

$v_g$ - phonon group velocity
$\tau$ - phonon relaxation time

\[ v_s = \sqrt{\frac{B}{d}} \]

$v_s$ - acoustic speed of sound
$B$ - elastic modulus
$d$ - density

New materials should have ‘soft’ bonding and be composed of heavy atoms
Designing low $\kappa_L$ materials - group velocity

$$\kappa_L = \frac{1}{3} \int C v_g^2 \tau d\omega$$

$v_g$ - phonon group velocity
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$$v_s = \sqrt{\frac{B}{d}}$$

$v_s$ - acoustic speed of sound
$B$ - elastic modulus
$d$ - density

$v_g(\omega) = v_s$
Valid only for phonons at long wavelengths!

$$v_g = \frac{\partial \omega}{\partial k}$$
Lattice thermal conductivity prediction

In complex materials:
- 3 acoustic branches (2 transverse, 1 longitudinal)
- 3(N-1) optical branches, where N is # atoms in primitive cell

$$\kappa_a = \frac{cM\theta_D^3 a}{N^{1/3} \gamma^2 T}$$

True in practice?

Slack, *Solid State Phys* 1979
Antimonides and thermal conductivity

Primitive unit cell complexity good indicator for $\kappa_L$

Yb$_{14}$Mn$_x$Al$_{1-x}$Sb$_{11}$ - Glass like thermal conductivity

Low $\kappa_L$ arises from:
Complexity ($N = 104$)
Density
Mass contrast
Anharmonicity ($\gamma = 1.5$)

No evidence of rattling:
Single crystal XRD thermal ellipsoids
Understanding thermal conductivity in Yb$_{14}$MnSb$_{11}$

$\nu_{optic}$ so low, we will use the theory developed for glassy materials.

\[ K_{optic} = K_{glass} \]

\[ K_{acoustic} = \frac{1}{3} \int_{0}^{\omega_{acoustic}} C \nu^2 \tau d\omega \]

\[ K_{lattice} = K_{acoustic} + K_{optic} \]

300K
Prediction: 0.8 W m$^{-1}$ K$^{-1}$
Reality: 0.6 W m$^{-1}$ K$^{-1}$
Figure of merit (zT) >1 at 1200K!

Factors contributing to good thermoelectric performance:

- Band gap (0.5 eV) and moderate mobility
- Robust carrier concentration control
- Glass-like $\kappa_L$

Zintl $Yb_{14}Mn_xAl_{1-x}Sb_{11}$ - Next generation power source

Figure of merit (zT) >1 at 1200K!

NASA has been flying $Si_{0.8}Ge_{0.2}$ for the last 30 years with a peak zT of 0.6 at 1100K.

JPL:
14-1-11/La$_{3-x}$Te$_4$ (BOL)
10% efficient at 1000°C
3000 hours of test

Segmented with skutterudite:
15% efficient (180/1000°C, BOL)
New Earth-abundant complex semiconductors

$\text{Ca}_5\text{Al}_2\text{Sb}_6$ ($N = 26$) and $\text{Ca}_3\text{AlSb}_3$ ($N = 28$):

Outline

\[ \kappa_L = \frac{1}{3} \int C v_g^2 \tau d\omega \]

Group velocity \( (v_g) \)
- Structural complexity
  - \( \text{Yb}_{14}\text{MnSb}_{11} \)
  - \( \text{Ca}_5\text{Al}_2\text{Sb}_6 \)
  - \( \text{Ca}_3\text{AlSb}_3 \)

Scattering \( (\tau) \)
- Intrinsic point defects
  - \( \text{La}_{3-x}\text{Te}_4 \)
  - \( \text{Zn}_4\text{Sb}_3 \)
- Nanostructures
  - \( \text{Zn}_4\text{Sb}_3 \)
  - \( \text{PbTe} \)
Scattering: Relevant phonon relaxation times

\[ \kappa_L = \frac{1}{3} \int C v_g^2 \tau d\omega \]

\[ \tau^{-1} = \sum_i \tau_{i}^{-1} \]

\[ \kappa_L = \int \kappa_{\text{spectral}} d\omega \]
Scattering: Relevant phonon relaxation times

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\[ \tau^{-1} = \sum_i \tau_i^{-1} \]

\[ \kappa_L = \int \kappa_{\text{spectral}} d\omega \]
La$_{3-x}$Te$_4$ - High T n-type material

Charge balance: $\text{La}_2^{3+}\text{Te}_3^{2-}$

Th$_3$P$_4$:

Conflict between structure type and charge balanced composition:
- vacancies!

Other sources of low $\kappa_L$:
- Anharmonicity (1.7)
- High density
- $N = 14$
- Moderately soft bonding
  $v = 3580$ (l) and 2010 (t) m/s

Cutler et al, Phys. Rev. (1964)

Delaire et al, Phys Rev B (2009)
Point defect scattering in Zn$_4$Sb$_3$

Like La$_{3-x}$Te$_4$, conflict between structure and charge balance

Structure: Zn$_{36}$Sb$_{30}$  Charge balance: Zn$_{39}$Sb$_{30}$

3 additional Zn - interstials

![Diagram](image)

$\text{Zn}_4\text{Sb}_3$

Like $\text{La}_{3-x}\text{Te}_4$, conflict between structure and charge balance

Structure: $\text{Zn}_{36}\text{Sb}_{30}$  Charge balance: $\text{Zn}_{39}\text{Sb}_{30}$

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Outline

\[ \kappa_L = \frac{1}{3} \int C v_g^2 \tau d\omega \]

Group velocity \((v_g)\)
- Structural complexity
  - \(Yb_{14}MnSb_{11}\)
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  - \(Ca_3AlSb_3\)

Scattering \((\tau)\)
- Intrinsic point defects
  - \(La_{3-x}Te_4\)
  - \(Zn_4Sb_3\)
- Nanostructures
  - \(Zn_4Sb_3\)
  - \(PbTe\)
Nanostructured $\text{Zn}_4\text{Sb}_3$

ZnSb precipitates (10nm) found in Sb rich samples of $\text{Zn}_4\text{Sb}_3$

Coherent Zn precipitates found in some samples of $\text{Zn}_4\text{Sb}_3$

PbTe-Ag$_2$Te Composite Formation

Ag$_2$Te precipitates form as expected from equilibrium phase diagram.

Nanoscale Effects

- Thermal conductivity reduction ~20%
- Must be reduced in matrix
- Reduction due to Nanoscale Effects
- even from ~100nm microstructure!

Outlook

Successful strategies for targeting low $\kappa_L$ materials must utilize both group velocity and scattering!

Group velocity: heavy materials, soft bonding, low velocity optical modes

Scattering: spontaneously formation of point defects and nanostructures

$\text{Yb}_{14}\text{MnSb}_{11}$

$\text{Ca}_3\text{AlSb}_3$

$\text{La}_{3-x}\text{Te}_4$

$\text{Zn}_4\text{Sb}_3$

$\text{PbTe}$
Acknowledgements

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- Jean-Pierre Fleurial and Thierry Callait (Jet Propulsion Laboratory)

Review articles:
Lattice thermal conductivity model

Debye Model:

\[ \kappa_L = \frac{1}{3} \int C(\omega) \nu_g(\omega)^2 \tau(\omega) d\omega \]

\[ \kappa_L = \frac{\hbar^2}{2\pi^2 k_B T^2} \int_0^{\omega_m} \frac{\omega^4 \exp[\hbar \omega / kT]}{\nu_p^2 \nu_g(\exp[\hbar \omega / kT] - 1)^2} d\omega \]

\[ C_v = \frac{3\hbar^2}{2\pi^2 k_B T^2} \int_0^{\omega_m} \frac{\omega^4 \exp[\hbar \omega / kT]}{\nu_p^2 \nu_g(\exp[\hbar \omega / kT] - 1)^2} d\omega \]

Scattering:

\[ \tau^{-1} = \sum_i \tau_i^{-1} \]

\[ \tau_U(\omega) = \frac{\bar{M} \nu_g \nu_p^2}{C \alpha \gamma^2 k \omega^2} \]

\[ \tau_{PD} = \frac{V}{4\pi \nu^3} \omega^4 \sum_i f_i \left( \frac{\bar{m} - m_i}{\bar{m}} \right)^2 \]

Cahill’s glass model:

\[ \kappa_g = \left( \frac{\pi}{6} \right)^{1/3} \frac{\hbar^4}{k_B^3 a^2 T^2} \sum_i \frac{\nu_i}{\Theta_i^2} \int_{\omega_p / n^{1/3}}^{\omega_D} \frac{\omega^3 \exp[\hbar \omega / kT]}{(\exp[\hbar \omega / kT] - 1)^2} d\omega \]
Understanding thermal conductivity in Yb$_{14}$MnSb$_{11}$

**Phonon mean free path ($l$):**

$$ l^{-1} = \sum_i l_i^{-1} $$

$$ l_{\text{Umklapp}}(\omega) = \frac{Mv_g^2v_p^2}{C\gamma^2k\omega^2} $$

$$ l_{\text{Boundary}}(\omega) = d $$

$$ d = 1 \text{ micron} $$

\[ \kappa_{\text{acoustic}} = \frac{1}{3} \int_0^{\omega_{\text{acoustic}}} Cvl\,d\omega \]

300 K
Prediction acoustic: 0.5 W m$^{-1}$ K$^{-1}$
Reality total: 0.6 W m$^{-1}$ K$^{-1}$
Thermal conductivity in Yb$_{14}$MnSb$_{11}$

Here, heat transport is treated as a random walk of energy on a lattice. Coupling constant between the harmonic oscillators estimated by \( v \).
Speed of sound ($v$)

Despite similar speed of sounds between PbTe and Yb$_{14}$MnSb$_{11}$, there are very different lattice thermal conductivities.

\[
v = \sqrt{\frac{B}{d}}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>Density ($d$) $g$ cm$^{-3}$</th>
<th>Speed ($v_M$) m/s</th>
<th>Lattice Thermal Conductivity ($\kappa_L$) $W m^{-1} K^{-1}$ (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe</td>
<td>8.2</td>
<td>1400</td>
<td>2.1</td>
</tr>
<tr>
<td>Yb$<em>{14}$MnSb$</em>{11}$</td>
<td>8.4</td>
<td>1600</td>
<td>0.6</td>
</tr>
</tbody>
</table>

PbTe (Fm-3m)  
Yb$_{14}$MnSb$_{11}$ (I4/ammc)
Yb$_{14}$AlSb$_{11}$

Cations: 14 Yb$^{2+}$

Isolated anionic moieties:
- AlSb$_4^{9-}$ tetrahedra
- Sb$_3^{7-}$ linear trimer
- 4 isolated Sb$^{3-}$

Intrinsic semiconductor due to precise valence balance
- Large, decreasing resistance with increasing T

104 atoms in the primitive cell.

Successful $p$-type doping with Mn$^{2+}$ alloying on Al$^{3+}$ site!

$Yb_{14}Mn_xAl_{1-x}Sb_{11}$ very metallic (linear resistivity with temperature)

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

\[ m^* = 3 \, m_e \]

Massive for a band conductor!

Beyond the confines of a single parabolic band model

Transport within a single parabolic band will only get us so far - need a new approach!

\[
\alpha = \frac{k}{e} \left( \frac{(2 + \lambda)F_{1+\lambda}(\eta)}{(1 + \lambda)F_{\lambda}(\eta)} - \eta \right)
\]

\[
F_r(\eta) = \int_0^\infty \zeta^r f_0(\eta) d\zeta
\]

\[
\mu_H = \frac{\mu_0 \pi^{1/2} F_{\lambda}(\eta)}{2\Gamma(1 + \lambda)F_{1/2}(\eta)}
\]

\[
n = \frac{4}{\sqrt{\pi}} \left( \frac{2\pi m^* kT}{\hbar^2} \right)^{3/2} F_{1/2}(\eta)
\]

\[
L = \left( \frac{k}{e} \right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_1(\eta)^2}{F_0(\eta)^2}
\]
Formation of band gaps in the phonon dispersion

1D chain of atoms coupled via spring ($K$):

\begin{align*}
\omega_{\text{max}} &= \sqrt{\frac{4K}{M}} \\
\omega_o &= \sqrt{\frac{2K}{M_2}} \\
\omega_a &= \sqrt{\frac{2K}{M_1}}
\end{align*}
Phonon dispersion for 1-D chain

This approach to

1D chain of atoms coupled via spring ($K$):

$$N = 1$$

$$\pi / a$$

$$\omega_{\text{max}} = \frac{4K}{M}$$

$$K_{\text{lattice}} = \frac{1}{3} C_v v l$$

Fine approximation, if $v$ is constant

$$v_g = \frac{\partial \omega}{\partial k}$$
Formation of band gaps in the phonon dispersion

1D chain of atoms coupled via spring ($K$):

\[ \omega_{\text{max}} = \sqrt{\frac{4K}{M}} \]

\[ \omega_{\text{o}} = \sqrt{\frac{2K}{M_2}} \]

\[ \omega_{\text{a}} = \sqrt{\frac{2K}{M_1}} \]
Thermal conductivity estimation

\[ \kappa_L = \frac{1}{3} \int C \nu_g^2 \tau \, d\omega \]

\( \nu_g \) - phonon group velocity
\( \tau \) - phonon relaxation time
Umklapp, point defect...

Assumptions:
1. Acoustic branch: Debye solid, optical branches: phonon glass
2. \( \tau \) dominated by Umklapp scattering

\[ \tau_{Umklapp} \propto T^{-1} \gamma^{-2} \]

Thermal conductivity estimation

\[ \kappa_L = \frac{1}{3} \int C \nu_g^2 \tau d\omega \]

- \( \nu_g \): phonon group velocity
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- Umklapp, point defect...

Assumptions:
1. Acoustic branch: Debye solid, optical branches: phonon glass
2. \( \tau \) dominated by Umklapp scattering

\[ \kappa_L = \frac{cM\theta_D^3 a}{N^{1/3} \gamma^2 T} \]

- \( M \): mass
- \( \theta_D \): Debye temperature
- \( \gamma \): Gruneisen parameter
- \( a \): interatomic distance
- \( N \): number of atoms in primitive cell

Recall \( \theta_D \propto M^{-1} \)

Good thermoelectric materials:
- heavy (low \( \theta_D \))
- anharmonic bonding (large \( \gamma \))
- structurally complex (large \( N \))

Search for improved materials

Want to satisfy 2 requirements:
1 - Degenerate semiconductor w/ large $m^{3/2}\mu$, high degeneracy
2 - Structural complexity to trap heat in low $\nu$ optical modes

But where?
Uses novel materials developed in last few years:
  • JPL and university collaborators
  • 14-1-11 Zintls, $\text{La}_{3-x}\text{Te}_4$, nano bulk Si-Ge, filled Skutterudites

First set of couples built and tested at JPL in March 2009
  • 10% efficient at 1000°C 14-1-11 Zintls/$\text{La}_{3-x}\text{Te}_4$ (BOL), 3000 hours of test

~6.3% Efficiency, 2.8 W/kg

Multi-Mission RTG (MSL)

Near Term Goal:
> 10% Efficiency, 6 W/kg

Longer Term Goal:
> 15% Efficiency, 10 W/kg
Validating strong N dependence in antimonides

Strip N dependence from equation, compare to experiment:

\[ \frac{\kappa_{L,\text{exp}}}{\kappa_{L,\text{calc}}} = \frac{\kappa_L \gamma^2 T}{cM \theta_D^3 a} \]

![Graph showing N dependence comparison between experiment and calculation, with data points for AlSb, GaSb, and InSb. The graph plots \( \frac{\kappa_L}{\kappa_{\text{calc}}} \) against N (atoms), with a trend line indicating \( N^{-1} \).]
Validating strong N dependence in antimonides

\[
\frac{\kappa_{L,\text{exp}}}{\kappa_{L,\text{calc}}} = \frac{\kappa_L \gamma^2 T}{c\bar{M}\theta_D^3 a}
\]

IrSb\textsubscript{3}

LiZnSb

Mo\textsubscript{3}Sb\textsubscript{7}

SrZn\textsubscript{2}Sb\textsubscript{2}

CeFe\textsubscript{4}Sb\textsubscript{12}

BaZn\textsubscript{2}Sb\textsubscript{2}

Ca\textsubscript{5}Al\textsubscript{2}Sb\textsubscript{6}

Mg\textsubscript{3}Sb\textsubscript{2}

SrZnSb\textsubscript{2}

Yb\textsubscript{11}Sb\textsubscript{10}

ZnSb

CdSb

Yb\textsubscript{11}GaSb\textsubscript{9}

Zn\textsubscript{4}Sb\textsubscript{3}

Yb\textsubscript{14}MnSb\textsubscript{11}

Yb\textsubscript{14}AlSb\textsubscript{11}

N dependence is strong!
Unsegmented & Segmented Couples Under Development at JPL (10-15% eff.):

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Segmented couples recently built, tested
- 14-1-11, $\text{La}_{3-x}\text{Te}_4$, segmented with filled Skutterudites
- >11% efficient at 800 C/200 C (BOL demonstration completed)
- >13% efficient at 1000 C/200 C (BOL demonstration completed)
- >15% efficient at 1000 C/200 C demonstration planned for 9/2011
Reassessment of PbTe thermal conductivity

Classic 1960s work prior to development of laser flash diffusivity
High temperature $\kappa$ was estimated!

Sources of low $\kappa_L$:
- Large Gruneisen parameter (1.5)
- High density
- Soft bonding
  $v = XXXX \ (l)$ and $YYyy \ (t) \ m/s$

Pei et al  Energy Env. Sci (2010) *in press*
Retrograde Solubility in Zn$_4$Sb$_3$

- Calculated phase diagram Zn$_x$Sb$_3$ ab initio
- Confirms Zn$_4$Sb$_3$ stable due to configurational and Vibrational Entropy
- Correctly predicts phase should be Zn poor = p-type

Zn Precipitates in Zn$_4$Sb$_3$

- Coherent Zn precipitates found in some samples of Zn$_4$Sb$_3$

Fundamental material parameters

\[ zT = \frac{\alpha^2 \sigma T}{\kappa} \quad \rightarrow \quad \beta = \frac{\mu m^*^{3/2}}{\kappa_L} \]

Conflicts:  Jeff Snyder’s talk: \[ \mu = \frac{e\tau}{m^*} \]

This talk: \( \kappa_L \gg \kappa_{glass} \)

How do we find materials which have \( \kappa_L \approx \kappa_{glass} \)?

Chasmar and Stratton (1959)
‘Simple’ example - PbTe thermal conductivity

PbTe known to have low $\kappa_L$ - why?

Sources of low $\kappa_L$:
- Large Gruneisen parameter (1.5)
- High density
- Soft bonding
  $\nu = XXXX (l)$ and $YYyy (t) \text{ m/s}$

- Increased Umklapp scattering
- Low $\nu_s$

No structural complexity
2 atoms in primitive cell
Outline

\[ \kappa_L = \frac{1}{3} \int C \nu_g^2 \tau \, d\omega \]

Group velocity (\( \nu_g \))
- Heavy atoms, soft bonding
  - PbTe
- Structural complexity
  - Yb\(_{14}\)MnSb\(_{11}\)
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- Intrinsic point defects
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