SUTTERITES FOR THERMOELECTRIC APPLICATIONS

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by

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Novel Thermoelectric Materials
State-of-the-art thermoelectric materials

$ZT = 1$ limit but much larger $\geq T$ values are theoretically possible
Applications of Improved Thermoelectric Materials

- Improved performance could open up wide market for thermoelectric devices
  - Power Generation
    - Waste heat recovery (automobile, industrial processes..)
    - Space Power (RTGs, microRTGs)
  - Cooling
    - Thermal management (high power electronic devices)
    - Air conditioning (ship, automobile..)
    - Refrigeration (consumer appliances..)
  - Sensors

Novel Thermoelectric Materials
Approaches to Find More Efficient New Thermoelectric Materials

Conventional semiconductors
- Binary compounds
- Ternary and more complex compounds

Unconventional semiconductors
- Non conventional transport properties

Heterostructures
- Superlattices
- Quantum wells

Novel Thermoelectric Materials
Current JPL Activities in Thermoelectrics

**Materials**

- Preparation, characterization, analysis and modeling of new thermoelectric materials
- Skutterudites, other compounds and alloys
- Measurement of transport properties of semiconductors
- 4K-1300K temperature range

**Devices**

- Testing of thermoelectric power generating devices
  - SP-100 multicouple cells

**Modeling**

- Modeling of transport properties
  - Computer models to predict ZT

**Novel Thermoelectric Materials**
New Materials: Exploratory Search

The search for thermoelectric materials with high ZT values is guided by a certain number of criteria, including:

- Semiconducting properties
- Large Seebeck coefficient
- High carrier mobility, high electrical conductivity
- Low lattice thermal conductivity
- Chemical stability and low vapor pressure
- Band gap > $4k_B T$ at operating temperature

Selection of high-performance thermoelectric materials necessitates striking a balance between conflicting requirements for the optimization of the various transport properties.
Existence of Skutterudites

- JPL Exploratory search identified skutterudite family
  Binary Compounds
  - Nine semiconducting and two metallic compounds
  Solid solutions
  - Found solid solutions exist between most binary skutterudites as well as in many other systems
  New phases are derived from binary compounds
  - By replacing the transition metal or the pnictogen or both elements
  - By conserving the number of valence electrons
  - Numerous related skutterudite phases exist

Filled skutterudites
- Literature data show that filled skutterudites can be formed
- By filling the two empty octants present in the 32 atoms unit cell
- The number of valence electrons needs to remain constant to conserve a semiconducting behavior

Novel Thermoelectric Materials
JPL Programs on Skutterudites
A Systematic Study in Progress

Investigating basic properties of skutterudites materials
- First study binary compounds
- Then ternary/quaternary isostructural phases

Conducting experimental and theoretical studies
- Decomposition temperature, atomic composition
- Band gap, Debye temperature, thermal expansion, Grüneisen constant
- Thermoelectric properties
  - Seebeck coefficient
  - Carrier mobility
  - Lattice thermal conductivity
  - Doping level

To obtain best compositions for maximum ZT
Skutterudite Crystal Structure

T: transition metal
O P.: pnictogen

Novel Thermoelectric Materials
Tools to Study Skutterudite Compositions

Materials preparation
- Single and polycrystalline samples
- From the melt (some binary compounds)
- Using powder metallurgy techniques (all other compounds)

Measurements: electrical and thermal transport properties
- Hall effect, electrical and thermal conductivities, Seebeck coefficient
- From 4K to 1200K

Analysis and modeling of variations in transport properties
- As a function of carrier concentration, temperature and composition
- Also using JPL model developed for several thermoelectric materials

Calculation of the electronic structure of skutterudites
- From first principles, using the tight-binding method
- Electronic structure of dopants, substituting atoms in skutterudites

Novel Thermoelectric Materials
Binary Skutterudite Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$T_m$ (°C)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoP$_3$</td>
<td>7.7073</td>
<td>&gt;1000</td>
<td>0.43*</td>
</tr>
<tr>
<td>CoAs$_3$</td>
<td>8.2043</td>
<td>960</td>
<td>0.69*</td>
</tr>
<tr>
<td>CoSb$_3$</td>
<td>9.0385</td>
<td>850</td>
<td>0.63*</td>
</tr>
<tr>
<td>RhP$_3$</td>
<td>7.9951</td>
<td>&gt;1200</td>
<td>-</td>
</tr>
<tr>
<td>RhAs$_3$</td>
<td>8.4427</td>
<td>&gt;1000</td>
<td>&gt;0.85*</td>
</tr>
<tr>
<td>RhSb$_3$</td>
<td>9.2322</td>
<td>900</td>
<td>0.80*</td>
</tr>
<tr>
<td>IrP$_3$</td>
<td>8.0151</td>
<td>&gt;1200</td>
<td>-</td>
</tr>
<tr>
<td>IrAs$_3$</td>
<td>8.4673</td>
<td>&gt;1200</td>
<td>-</td>
</tr>
<tr>
<td>IrSb$_3$</td>
<td>9.2533</td>
<td>1141*</td>
<td>1.18*</td>
</tr>
<tr>
<td>NiP$_3$</td>
<td>7.819</td>
<td>&gt;850</td>
<td>metallic</td>
</tr>
<tr>
<td>PdP$_3$</td>
<td>7.705</td>
<td>&gt;650</td>
<td>metallic</td>
</tr>
</tbody>
</table>

* JPL findings
Binary Skutterudites
300K Hall Mobility

Novel Thermoelectric Materials
Binary Skutterudites: CoSb₃
300K Electrical Resistivity

Novel Thermoelectric Materials
Binary Skutterudites: CoSb$_3$
300K Hall Mobility

Novel Thermoelectric Materials
Binary Skutterudites: CoSb₃
300K Seebeck Coefficient

Novel Thermoelectric Materials
Binary Skutterudites: P-Type CoSb$_3$
Electrical Resistivity vs. T

Novel Thermoelectric Materials
Binary Skutterudites P-Type CoSb₃
Seebeck Coefficient v. s. T

Novel Thermoelectric Materials
Binary Skutterudites: P-Type CoSb$_3$

Hall Mobility vs. T

![Graph showing Hall mobility vs. temperature for p-type CoSb$_3$.]
Binary Skutterudites: N-Type CoSb$_3$
Electrical Resistivity vs. T
Binary Skutterudites: N-Type CoSb₃
Seebeck Coefficient vs. T
Binary Skutterudites: N-Type CoSb₃
Hall Mobility vs. T
Power factor values for n- and p-type CoSb$_3$ at 300K

Power factor = $\alpha^2 \sigma$

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Binary Skutterudites: $\text{CoSb}_3$
Thermal Conductivity vs. $T$

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Electron-phonon scattering mechanism in heavily doped n-type CoSb$_3$
Binary Skutterudites
Hall Mobility vs. T

p-type conductivity, at various carrier concentrations

Novel Thermoelectric Materials
Summary on Binary Skutterudites

- High temperature band gap values: 0.4 - 1.2 eV
  - Possibility of CoSb$_3$, IrSb$_3$ being zero-band gap semiconductors
  - Possibility of unusual non-parabolicity for valence band
- P-type electrical properties
  - Very high mobilities, low electrical resistivities
    - Due to small effective masses (~ 0.1 m$_o$)
  - Moderate p-type Seebeck coefficients (100-200 µV.K$^{-1}$)
- N-type electrical properties
  - N-type mobilities are lower but still reasonable
    - Due to large effective masses (~ 1.5 m$_o$)
  - Large n-type values (200-600 µV.K$^{-1}$)

Thermal conductivities are moderate
- But too high for thermoelectric applications

Large family of isostructural semiconductors
- N-type skutterudites might result in higher T/E performance

Need for reductions in lattice thermal conductivity

Novel Thermoelectric Materials
Ternary Compounds and Phases Derived from Binary Skutterudites

New compounds/phases are derived from binary compounds
- By replacing the transition metal or the anionic or both elements
- By conserving the number of valence electrons

Our results (and literature data) show that numerous related skutterudite phases exist
- We know of 23 ternary phases, 14 new ones found at JPL.

Transport properties can change dramatically
- Increased atomic disorder, changes in band structure, doping, and scattering mechanisms
- All new ternary compound characterized at JPL have low thermal conductivity (7 to 35 mW/cm.K)
- Each new phase should be separately characterized
- If promising, solid solutions are also considered
Ternary Compounds and Phases Derived from Binary Skutterudites

Related Phases Based on Skutterudite Binary Compound (CoSb$_3$)

- Replace Co to get Fe$_{0.5}$Ni$_{0.5}$Sb$_3$
  - Co
  - Fe$_{0.5}$
  - Ni$_{0.5}$
  - Sb$_3$

- Replace Sb to get CoGe$_{1.5}$Se$_{1.5}$
  - Co
  - Ge$_{1.5}$
  - Se$_{1.5}$
  - Sb$_3$

- Replace Co and Sb to get RuSb$_2$Te or PtSnSb$_2$
  - Co
  - Ru
  - Pt
  - Sn
  - Sb$_2$
  - Te

Novel Thermoelectric Materials
## Ternary Skutterudite Phases

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>Tm (°C)</th>
<th>Compound</th>
<th>a (Å)</th>
<th>Tm (°C)</th>
<th>Es (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoGe\textsubscript{1.5}S\textsubscript{1.5}</td>
<td>8.017</td>
<td>1000</td>
<td>Fe\textsuperscript{2+}Sb\textsuperscript{2+}</td>
<td>0.0004</td>
<td>779*</td>
<td>~0.16*</td>
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<tr>
<td>CoGe\textsubscript{1.5}Se\textsubscript{1.5}</td>
<td>8.299</td>
<td>800</td>
<td>Fe\textsuperscript{2+}P\textsuperscript{3+}Se\textsuperscript{2+}</td>
<td>0.7060*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoGe\textsubscript{0.5}Te\textsubscript{0.5}</td>
<td>&gt; 800</td>
<td></td>
<td>P\textsuperscript{2+}Sb\textsuperscript{2+}</td>
<td>0.1050*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoS\textsubscript{0.5}Se\textsubscript{0.5}</td>
<td></td>
<td></td>
<td>R \textsuperscript{2+}Sb\textsuperscript{3+}</td>
<td>0.1580*</td>
<td>647*</td>
<td>~0.60*</td>
</tr>
<tr>
<td>Co\textsuperscript{2+}Se\textsuperscript{2+}</td>
<td>8.2746</td>
<td>&gt; 800</td>
<td>Fe\textsubscript{2+}Fe\textsubscript{2+}Te\textsuperscript{2+}</td>
<td>9.112*</td>
<td>556*</td>
<td>~0.27*</td>
</tr>
<tr>
<td>RhGe\textsubscript{1.5}S\textsubscript{1.5}</td>
<td>8.297</td>
<td>&gt; 800</td>
<td>Fe\textsubscript{2+}N\textsubscript{2+}A\textsubscript{2+}</td>
<td>12.76</td>
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<tr>
<td>IrGe\textsubscript{1.5}S\textsubscript{1.5}</td>
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<td>&gt; 800</td>
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<td>9.268*</td>
<td>810*</td>
<td>1.20*</td>
</tr>
<tr>
<td>Ir\textsuperscript{2+}Te\textsuperscript{2+}</td>
<td>9.7050</td>
<td>&gt; 800</td>
<td>RuSb\textsubscript{2+}Te\textsuperscript{2+}</td>
<td>9.757*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ir\textsuperscript{2+}Sb\textsuperscript{2+}</td>
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<td></td>
<td>Os\textsuperscript{2+}Sb\textsuperscript{2+}</td>
<td>1.908*</td>
<td>~800</td>
<td>-</td>
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<tr>
<td>P\textsuperscript{2+}Sn\textsuperscript{2+}Sb</td>
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<td></td>
<td>P\textsuperscript{2+}Pb\textsuperscript{2+}</td>
<td>7.9040</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>NiGe\textsubscript{2+}</td>
<td></td>
<td></td>
<td>Ni\textsuperscript{2+}B\textsuperscript{2+}</td>
<td>0.440</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

* JPL findings

**Novel Thermoelectric Materials**
Lattice thermal conductivity reduction due to electron charge transfer in ternary compounds: Ru$_{0.5}$Pd$_{0.5}$Sb$_3$
Solid Solutions and Alloys Derived from Binary and Ternary Skutterudites

To form solid solutions is a well-known approach
- All state-of-the-art thermoelectric materials are solid solutions
- Solid solutions exist between most binary skutterudites
  - CoSb$_3$-IrSb$_3$: 110 mW/cmK; Co$_{0.12}$Ir$_{0.88}$Sb$_3$: 28 mW/cmK
  - CoAs$_2$-CoSb$_3$; CoP$_3$-CoAs$_3$; IrAs$_2$-IrSb$_3$

Found solid solutions exist in many other systems, such as:
- CoSb$_3$-Ru$_{0.5}$Pd$_{0.5}$Sb$_3$
- IrSb$_3$-RuSb$_2$Te
- Fe$_{0.5}$Ni$_{0.5}$Sb$_3$-Ru$_{0.5}$Pd$_{0.5}$Sb$_3$

Reductions in lattice thermal conductivity, carrier mobility
- Should only need a few selected compositions to predict $ZT_{\text{max}}$

N-type compositions are promising
- Currently working on them

Nove Thermoelectric Materials
# Skutterudite Solid Solutions

<table>
<thead>
<tr>
<th>Solid Solutions</th>
<th>Partial Range of Compositions</th>
<th>Full Range of Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoP$_3$</td>
<td></td>
<td>CoAs$_3^*$</td>
</tr>
<tr>
<td>CoAs$_3$</td>
<td>CoSb$_3^*$, IrAs$_3$</td>
<td></td>
</tr>
<tr>
<td>CoSb$_3$</td>
<td>CoAs$<em>3^*$, Fe$</em>{0.5}$Ni$_{0.5}$Sb$_3$, FeSb$_2$Te, FeSb$_2$Se</td>
<td>IrSb$_3$</td>
</tr>
<tr>
<td>RhSb$_3$</td>
<td></td>
<td>IrSb$_3$</td>
</tr>
<tr>
<td>IrAs$_3$</td>
<td>CoAs$_3$, IrSb$_3$</td>
<td></td>
</tr>
<tr>
<td>IrSb$_3$</td>
<td>CoSb$<em>3$, IrAs$<em>3$, Fe$</em>{0.5}$Ni$</em>{0.5}$Sb$_3$</td>
<td>RhSb$_3$, RuSb$_2$Te</td>
</tr>
<tr>
<td>Fe$<em>{0.5}$Ni$</em>{0.5}$Sb$_3$</td>
<td>CoSb$_3$, IrSb$_3$</td>
<td>Ru$<em>{0.5}$Pd$</em>{0.5}$Sb$_3$</td>
</tr>
<tr>
<td>Ru$<em>{0.5}$Pd$</em>{0.5}$Sb$_3$</td>
<td>CoSb$_3$, IrSb$_3$</td>
<td>Fe$<em>{0.5}$Ni$</em>{0.5}$Sb$_3$</td>
</tr>
<tr>
<td>FeSb$_2$Te</td>
<td>CoSb$_3$, RuSb$_2$Te</td>
<td></td>
</tr>
<tr>
<td>RuSb$_2$Te</td>
<td>FeSb$_2$Te</td>
<td>IrSb$_3$</td>
</tr>
</tbody>
</table>

*literature results

*Novel Thermoelectric Materials*
**Filled Skutterudites**

- Literature data show that filled skutterudites can be formed
  - Using rare earth elements such as La or Ce in a Fe₈P₁₂ frame
  - But most of them were metal "c"

Preparation of filled skutterudites from binary compounds
- By filling the two empty octants present in the 32 atoms unit cell
- With a heavy element such as Bi, Pb or Y
- The number of valence electrons needs to remain constant to conserve a semiconducting behavior

Study compositions derived from filled skutterudites
- By substitution on the transition metal or pnictogen site
- To compensate for the p-type metallic character

These approaches could substantially lower the lattice thermal conductivity values
- "rattling" atom in octant "cage"
- Expect only slight reduction in carrier mobility

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Filled Skutterudites Derived from Binary Compounds

Filled Skutterudites Based on Skutterudite Binary Compound \([\text{IrSb}_3]\)

- **Filling Atom: Bi**
  - Compensating Atom: Ru
  - Ru Substitutes for Ir

- **Filling Atom: Pb**
  - Compensating Atom: Ge
  - Ge Substitutes for Sb

- \(\text{Ir}_8\)
- \(\text{Sb}_{24}\)
- \([\text{empty octant}]_2\)

- \(\text{Ir}_8\)
- \(\text{Sb}_{24}\)
- \([\text{Bi}+3]_2\)

- \(\text{Ir}_8\)
- \((\text{Ge}-1)_4\)
- \(\text{Sb}_{20}\)
- \([\text{Pb}+2]_2\)

*Novel Thermoelectric Materials*
Results on Ternary Skutterudites, Alloys and Filled Skutterudites

Ternary skutterudites compounds
- Most are p-type semiconductors
  - With high carrier concentrations
- Reasonably good Hall mobilities
- Moderate to low p-type Seebeck coefficients (100-200 µV.K⁻¹)
  - Surprisingly low thermal conductivity
    - Cannot be explained from point defect scattering (compared to binaries)
    - Other phonon scattering mechanisms at work
      - Such as valence fluctuations, charge exchanges

Skutterudite alloys
- Both p-type and n-type can be obtained
- Goal is to maximize mass and volume fluctuations

Filled skutterudites
- Preliminary results indicate interesting thermoelectric properties
- Metallic behavior, but low thermal conductivity and good Seebeck

Novel Thermoelectric Materials
Electrical Resistivity of Skutterudites
Seebeck Coefficient of Skutterudites

Novel Thermoelectric Materials
Thermal Conductivity of Skutterudites

Novel Thermoelectric Materials
Skutterudite Solid Solutions: Thermal Conductivity Reductions (calculated)

Novel Thermoelectric Materials
Current Focus of JPL Programs

- Understand variations of general properties of skutterudites
  - With composition
  - With doping level and temperature

Focus is on ternary skutterudites and related phases
- Remaining binary compounds (mostly phosphides) difficult to prepare
- Thermal conductivity of binary skutterudites too high
- Thermal conductivity of ternary compounds and alloys much lower

Study of n-type materials of particular interest
- Because of their large Seebeck
- But requires high doping levels

Study of filled skutterudites also promising
- Because of their low thermal conductivity
- Approach can be combined with alloys

Novel Thermoelectric Materials
Conclusion

Exploratory search at JPL for new high performance thermoelectric materials identified skutterudite family
- Skutterudites might also be of interest for electronics, other applications
- Several skutterudites have shown very interesting properties
  - Very low thermal conductivity semiconductors
  - Very high p-type mobility values
  - Large n-type Seebeck values
  - Large number of isostructural materials
- Systematic investigation of skutterudites
  - Necessary to understand trends in properties
  - Goal is to determine best approach for high ZT

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