Thermoelectric Properties in the TiO$_2$/SnO$_2$ System

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Nanotechnology has provided a new interest in thermoelectric technology. A thermodynamically driven process is one approach in achieving nanostructures in bulk materials. TiO$_2$/SnO$_2$ system exhibits a large spinodal region with exceptional stable phase separated microstructures up to 1400 °C. Fabricated TiO$_2$/SnO$_2$ nanocomposites exhibit n-type behavior with Seebeck coefficients greater than -300 V/K. Composites exhibit good thermal conductance in the range of 7 to 1 W/mK. Dopant additions have not achieved high electrical conductivity (<1000 S/m). Formation of oxygen deficient composites, TixSn1-xO$_2$-y, can change the electrical conductivity by four orders of magnitude. Achieving higher thermoelectric ZT by oxygen deficiency is being explored. Seebeck coefficient, thermal conductivity, electrical conductance and microstructure will be discussed in relation to composition and doping.
Thermoelectric Properties in the TiO$_2$/SnO$_2$ System

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**Objective:** High Conversion Efficiency
- Reduces Mass, Volume & Cost

**Heat to Electric Power Generation**

- **Waste Heat to Power**
  - Waste Heat is an underutilized energy resource
  - U.S.-energy consumption ~29 tera-kWh \((10^{12})\)
    - Barrels of Oil – 170 giga-barrels \((10^9)\)
  - World-energy consumption ~120 tera- kWh \((10^{12})\)
  - 20-65 percent is lost in the form of heat
  - Maximizes efficiency
  - Reduces CO\(_2\) emission

- High temperature
- Oxidizing environment
- Low mass
- Low cost

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**Space Power Generation**

- **Specific Power (W/kg)**
  - \(ZT_{ave} \sim 2.0\)
  - \(ZT_{ave} \sim 1.1\) 2x Improvement
  - \(ZT_{ave} \sim 1.6\) 3x Improvement
  - \(ZT_{ave} \sim 0.75\) Nano Si-Ge
  - \(ZT_{ave} \sim 0.88\) Zintl/Nano Si-Ge
  - \(ZT_{ave} \sim 0.55\) RTG Si-Ge

- **Conversion Efficiency (%)**
  - 4
  - 6
  - 8
  - 10
  - 12
  - 14
  - 16
  - 18

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**Legend:**
- **Load**
- **Thot**
- **Thcold**
- **Voltage**
- **n-type**
- **p-type**
- **h+**
- **e-**
- **h-**

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**Notes:**
- Navy Blue (p-type) and Brown (n-type) electrons move across the load.
- Blue (n-type) and red (p-type) holes move across the load.
- The red heat source is connected to the cold side of the device.
- The blue heat source is connected to the hot side of the device.

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**Image Credits:**
- National Aeronautics and Space Administration (NASA)
Nanotechnology

Figure of Merit

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

- \( S \): Seebeck coefficient
- \( \sigma \): electrical conductivity
- \( \kappa \): thermal conductivity

Efficiency

\[ \eta_{\text{max}} = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_{\text{cold}}/T_{\text{hot}}} \]

Phonon Scattering:
- Atom disorder
- Superlattices
- Superlattices
- Crystal Structures
- Nano-technology

Fleurial/Chen – JPL/MIT

Si/Ge

Alloy Limit
Spinodal Decomposition

**Desired Features**
- ~50 nm grains
- High Temperature Stability
- Wide Composition Range
- Large $\Delta$ Mass

**Transparent Conducting Oxides**

*Insulator/Semiconductor/Conductor*
- Large Bandgap 2.4-3.8 ev
- N-type –Degenerate Semiconductor

<table>
<thead>
<tr>
<th>TCO</th>
<th>$\sigma$(S/m) @ RT</th>
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<tbody>
<tr>
<td>ITO</td>
<td>$8 \times 10^5$</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>$2.5 \times 10^5$</td>
</tr>
<tr>
<td>ZnO</td>
<td>$8.3 \times 10^5$</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>$7.7 \times 10^4$</td>
</tr>
<tr>
<td>CdSnO$_2$</td>
<td>$7.7 \times 10^5$</td>
</tr>
<tr>
<td>CdO:In</td>
<td>$1.7 \times 10^6$</td>
</tr>
</tbody>
</table>

**Electrical Conductivity**

ZnO:Al
ZT~0.6 @ 1000 °C

**Fig. 10.** TEM image of (Ti$_{0.5}$/Sn$_{0.5}$)$_2$O$_3$ ceramics annealed for 48 h.
Shultz & Stubican, JACS, 53, 1970
### Experimental

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity</th>
<th>APS</th>
<th>SSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>99.9%</td>
<td>50 nm</td>
<td>14.2 m²/g</td>
</tr>
<tr>
<td>TiO₂ Rutile</td>
<td>99.99%</td>
<td>20 nm, 30 m²/g</td>
<td></td>
</tr>
<tr>
<td>Dopants</td>
<td>CoO, MnO₂, Ta₂O₅, In₂O₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TiO₂/SnO₂**
- 50/50 mol %
- 75/25 mol %
- 25/75 mol %

**Powder Mixing**

**Compaction Die Press**

**Reactive Sintering**
- 1250-1550 °C

**Anneal**
- 72 Hrs

### Thermal Conductivity

- Laser Flash Method- Thermal Diffusivity
- Standard
- Specific Heat- $C_p$ - Laser Flash
- Thermal Conductivity ($K = \alpha pC_p$)

**Seebeck/Resistivity**

**ZEM-3**

ΔT 0-50 °C/Furnace RT-1000 °C

6-22 mm

4-8 mm
Sintering

50/50 TiO₂/SnO₂  
1625 °C

75/25 TiO₂/SnO₂  
1550 °C

SnO₂ Sintering-Inhibited
• Surface Diffusion <1100 °C
• Evaporation >1100 °C
SnO₂ → SnO + ½O₂ (g)

Sintering Aids-SnO₂
• MnO, CoO, CuO, ZnO

CoO → Co⁰⁰ Ti,Sn + V⁰⁰ O

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids

Ta₂O₅ → 2Ta°Ti,Sn + 2e° + ½O₂
In₂O₃ → 2In°Ti,Sn + 2V° O

50/50 TiO₂/SnO₂
Phase Separation

100 nm

1000

1100

1200

1300

1400

Densification

Sintering Controlled By SnO₂

50/50 TiO₂/SnO₂
75/25 TiO$_2$/SnO$_2$

- Undoped
- Large Grain
- Small Grain
- Nano-ppts
- Diffuse Composition Fluctuation
- 1% Ta$_2$O$_5$
Thermal Conductivity

- Compositions exhibit low $\kappa$ – 1.7 to 6.8 W/mK
- Observe no dependence on composition or post treatments
- Spinodal Decomposition – $\kappa$ reduction?
- Best ZT $\sim$ 0.05

Compositions

- 1% MnO-50 TiO$_2$
- 1% CoO-50 TiO$_2$
- 1% MnO-75 TiO$_2$
- 1% CoO-75 TiO$_2$
- 1% MnO-25 TiO$_2$
- 1% CoO-25 TiO$_2$
- 1% Ta$_2$O$_5$/0.5% CoO-25 TiO$_2$
Electrical Conductivity
75/25 TiO₂/SnO₂

- Ta₂O₅ & Nb₂O₅ - Increases σ
- No further σ increase above 2% dopant.
- In₂O₃, MnO & CoO – No σ increase

Activation Energy

<table>
<thead>
<tr>
<th></th>
<th>Undoped</th>
<th>1% Nb₂O₅</th>
<th>0.5% Ta₂O₅</th>
<th>0.5% Ta₂O₅</th>
<th>1% In₂O₃</th>
<th>1% Ta₂O₅</th>
<th>2% Ta₂O₅</th>
<th>4% Ta₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ (S/m)</td>
<td>0.97 ev</td>
<td>0.25 ev</td>
<td>0.49 ev</td>
<td>0.22 ev</td>
<td>0.99 ev</td>
<td>0.30 ev</td>
<td>0.26 ev</td>
<td>1.6 ev</td>
</tr>
<tr>
<td>1000/T (K⁻¹)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

ZT = \( \frac{S^2 \sigma}{kT} \)

σ to low
Seebeck Coefficient
75/25 TiO$_2$/SnO$_2$

- N-type
- Large Seebeck coefficients at low $\sigma$
- Increase Ta$_2$O$_5$ conc. reduces Seebeck coefficient
- Nb$_2$O$_5$ doping most effective in Seebeck reduction
Semiconductor

• Improve electrical conductivity by forming oxygen deficient material (Ti$_x$Sn$_{1-x}$)O$_{2-y}$
  \[(Ti_{0.5}Sn_{0.5})O_{2-y}\]

- H$_2$ Reduction, 10$^3$ to 10$^4$ x

• Control the oxygen stoichiometry to increase $\sigma$ and maintain a good Seebeck coefficient?
Effects of reducing conditions
\((\text{Ti}_{0.75}\text{Sn}_{0.25})\text{O}_{2-x}\)

4% Ta

1% Ta
Mechanical Robustness

Undoped – 800 °C

1% Ta doped – 900 °C

4% Ta doped – 900 °C
Power Factor and Thermal conductivity

\[ PF = S^2 \sigma \]

4% Ta₂O₅-800 °C
In Summary

• TiO$_2$/SnO$_2$ compositions exhibit low thermal conductivity. Nanostructured phases are observed.
• Improved electrical conductivity is observed for Ta$_2$O$_5$ doped (Ti$_{0.75}$Sn$_{0.25}$)O$_{2-x}$ reduced at 800 °C.
• Reduction of doped samples retained a low thermal conductivity ($\approx$2W/mK).
• 800 °C reduction increases the power factor by 1.69 – 2.76 for 4% Ta$_2$O$_5$ doping. However, ZT is <0.1.

Dense specimens with Sn-rich compositions need to be evaluated

Acknowledgements
Thomas Sabo
Raymond Babuder
Electrical Conductivity

$\text{(Ti}_{0.75}\text{Sn}_{0.25})\text{O}_{2-x}$

- $\geq 800 \, ^\circ\text{C}$ treatment is required to enhance $\sigma$.
- $4\% \, \text{Ta}_2\text{O}_5$ produces the highest $\sigma$.
- Significant effect on low temperature $\sigma$.

- $4\% \, \text{Ta}_2\text{O}_5$
- $2\% \, \text{Ta}_2\text{O}_5$
- $1\% \, \text{Ta}_2\text{O}_5$
- $1\% \, \text{Nb}_2\text{O}_5$