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 mV/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, Ti$_x$Sn$_{1-x}$O$_{2-y}$, 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 TiO₂/SnO₂ System

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

Heat to Electric Power Generation

- 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

Space Power Generation

Conversion Efficiency (%) vs. Specific Power (W/kg)
Nanotechnology

Figure of Merit

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

- \( S \) - Seebeck coefficient
- \( \sigma \) - electrical conductivity
- \( K \) - 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
- Alloying
- Crystal Structures
- Anharmonic vibrations
- Nano-technology

Fleurial/Chen – JPL/MIT

Si/Ge

Alloy Limit
Spinodal Decomposition

**Desired Features**

- ~50 nm grains
- High Temperature Stability
- Wide Composition Range
- Large Δ Mass

**Electrical Conductivity**

<table>
<thead>
<tr>
<th>TCO</th>
<th>$\sigma$ (S/m)  @ RT</th>
</tr>
</thead>
<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>

**Transparent Conducting Oxides**  
*Insulator/Semiconductor/Conductor*

- Large Bandgap 2.4-3.8 ev
- N-type – Degenerate Semiconductor

**Coherent Nucleation & Growth**

**Shultz & Stubican, JACS, 53, 1970**

**Fig. 10. TEM image of (Ti$_{0.8}$/Sn$_{0.2}$)$_2$O$_3$ ceramics annealed for 48 h.**
**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, 20 nm</td>
<td>&gt;30 m²/g</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 ($K = \alpha \rho C_p$)

**Seebeck/Resistivity**
- ZEM-3
- 6-22 mm
- 4-8 mm

$\Delta T$ 0-50 °C/Furnace RT-1000 °C
Sintering

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

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

CoO → Co⁺⁺_{Ti,Sn} + Vⁿ⁻⁻_{O^*}

50/50 TiO₂/SnO₂
1625 °C

75/25 TiO₂/SnO₂
1550 °C

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids
Ta₂O₅ → 2Ta⁺⁺_{Ti,Sn} + 2e⁻ + ½O₂

In₂O₃ → 2In⁺⁺_{Ti,Sn} + 2V_{O^*}
75/25 TiO$_2$/SnO$_2$

**Undoped**
- Large Grain
- Small Grain
- Nano-ppts
- Diffuse Composition Fluctuation

**1% Ta$_2$O$_5$**
Thermal Conductivity

Compositions

- 1% MnO-50 TiO₂
- 1% CoO-50 TiO₂
- 1% MnO-75 TiO₂
- 1% CoO-75 TiO₂
- 1% MnO-25 TiO₂
- 1% CoO-25 TiO₂
- 1% Ta₂O₅/0.5% CoO-25 TiO₂

- Compositions exhibit low κ – 1.7 to 6.8 W/mK
- Observe no dependence on composition or post treatments
- Spinodal Decomposition – κ reduction?
- Best ZT ~ 0.05
Electrical Conductivity
75/25 TiO₂/SnO₂

- Ta₂O₅ & Nb₂O₅ - Increases σ
  \[ M₂O₅ = 2M^\bullet_{Ti,Sn} + 2e^- + \frac{1}{2}O₂ + 4O^X_0 \]
- No further σ increase above 2% dopant.
- In₂O₃, MnO & CoO – No σ increase

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

<table>
<thead>
<tr>
<th>Doping</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.97 ev</td>
</tr>
<tr>
<td>1% Nb₂O₅</td>
<td>0.25 ev</td>
</tr>
<tr>
<td>0.5% Ta₂O₅</td>
<td>0.49 ev</td>
</tr>
<tr>
<td>4% Nb₂O₅</td>
<td>0.20 ev</td>
</tr>
<tr>
<td>1% Ta₂O₅</td>
<td>0.22 ev</td>
</tr>
<tr>
<td>1% In₂O₃</td>
<td>0.99 ev</td>
</tr>
<tr>
<td>2% Ta₂O₅</td>
<td>0.30 ev</td>
</tr>
<tr>
<td>1% CoO</td>
<td>1.6 ev</td>
</tr>
<tr>
<td>4% Ta₂O₅</td>
<td>0.26 ev</td>
</tr>
<tr>
<td>1% MnO</td>
<td>7.9 ev</td>
</tr>
</tbody>
</table>
Seebeck Coefficient

75/25 TiO₂/SnO₂

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

• Improve electrical conductivity by forming oxygen deficient material \((Ti_xSn_{1-x})O_{2-y}\)
  \((Ti_{0.5}Sn_{0.5})O_{2-y}\)

\(~0~\text{Seebeck Coefficient}\)

\(\sigma (S/m)\)

\(\frac{1}{T} (K^{-1})\)

\(\text{H}_2 \text{ Reduction}\)

\(10^3 \text{ to } 10^4 \times\)

\(\text{Temp. (°C)}\)

\(\text{Seebeck (µV/K)}\)

• 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

**Power Factor**

\[ PF = S^2 \sigma \]

- **4% Ta_2O_5-800 °C**

**Thermal Conductivity**

- Undoped-900 °C
- Undoped

**Graphical Representation**

- Temperature vs. Power Factor
- Temperature vs. Thermal Conductivity
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 (≈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

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

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