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-xO2-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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Heat to Electric Power Generation

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

Specific Power (W/kg) vs. Conversion Efficiency (%)
- ZTave ~2.0
- ZTave ~1.1, 2x Improvement
- ZTave ~1.6, 3x Improvement
- ZTave ~0.75, Nano Si-Ge
- ZTave ~0.88, Zintl/Nano Si-Ge
- ZTave ~0.55, RTG Si-Ge

Waste Heat to Power
- Waste Heat is a under utilized 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 CO₂ emission

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

Figure of Merit

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

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

Efficiency

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

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 $\Delta$ Mass

Transparent Conducting Oxides

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

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>

ZnO:Al
$ZT \sim 0.6$ @ 1000 °C

Fig. 10. TEM image of (Ti$_{0.8}$/Sn$_{0.2}$)O$_2$ ceramics annealed for 48 h.
Shultz & Stubican, JACS, 53, 1970
**Experimental**

### Materials

- **SnO₂**
  - Purity: 99.9%
  - APS: 50 nm
  - SSA: 14.2 m²/g

- **TiO₂ Rutile**
  - Purity: 99.99%
  - APS: 20 nm
  - SSA: > 30 m²/g

- **Dopants**
  - CoO, MnO₂, Ta₂O₅, In₂O₃

### Processes

- **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 - Cₚ - Laser Flash
- Thermal Conductivity (K = αρCₚ)

### Measurements

- **Seebeck/Resistivity**
  - ZEM-3

- **Thermal Conductivity**
  - ΔT 0-50 °C/Furnace RT-1000 °C
Sintering

50/50 TiO₂/SnO₂  1625 °C
75/25 TiO₂/SnO₂  1550 °C

SnO₂ Sintering-Inhibited
• Surface Diffusion <1100 °C
• Evaporation >1100 °C
\[ \text{SnO}_2 \to \text{SnO} + \frac{1}{2}\text{O}_2(g) \]

Sintering Aids-SnO₂
• MnO, CoO, CuO, ZnO
\[ \text{CoO} \to \text{Co}_{Ti,Sn}'' + V'O'' \]

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids
\[ Ta_2O_5 \to 2Ta_{Ti,Sn} + 2e^- + \frac{1}{2}O_2 \]
\[ In_2O_3 \to 2In_{Ti,Sn} + 2V_O^* \]
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 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$_2$

- 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
Electrical Conductivity
75/25 TiO₂/SnO₂

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

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

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 \((\text{Ti}_x\text{Sn}_{1-x})\text{O}_{2-y}\)

\[(\text{Ti}_{0.5}\text{Sn}_{0.5})\text{O}_{2-y}\]

• Control the oxygen stoichiometry to increase \(\sigma\) and maintain a good Seebeck coefficient?

\[\text{H}_2\text{ Reduction} \quad 10^3 \text{ to } 10^4 \text{ x} \]

\[\text{~0 Seebeck Coefficient} \]

\(\sigma (\text{S/m})\)

\(1/T (\text{K}^{-1})\)

\(\text{Temp. (oC)}\)

\(\text{Seebeck (\mu V/K)}\)
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% \( \text{Ta}_2\text{O}_5 \)-800 °C
In Summary

- TiO₂/SnO₂ compositions exhibit low thermal conductivity. Nanostructured phases are observed.
- Improved electrical conductivity is observed for Ta₂O₅ doped (Ti₀.₇₅Sn₀.₂₅)O₂₋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% Ta₂O₅ doping. However, ZT is <0.1.

Dense specimens with Sn-rich compositions need to be evaluated

Acknowledgements
Thomas Sabo
Raymond Babuder
Electrical Conductivity
$(Ti_{0.75}Sn_{0.25})O_{2-x}$

- ≥800 °C treatment is required to enhance $\sigma$.
- 4% Ta$_2$O$_5$ produces the highest $\sigma$.
- Significant effect on low temperature $\sigma$.

$4\%$ Ta$_2$O$_5$

$2\%$ Ta$_2$O$_5$

$1\%$ Ta$_2$O$_5$

$1\%$ Nb$_2$O$_5$