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 TiO₂/SnO₂ System

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Heat to Electric Power Generation

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

Space Power Generation
- Specific Power (W/kg)
- Conversion Efficiency (%)
- ZTave ~ 2.0
- 2x Improvement
- ZTave ~ 1.6
- 3x Improvement
- ZTave ~ 1.1
- 2x 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

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

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>8x10^5</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>1x10^6</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>2.5x10^5</td>
</tr>
<tr>
<td>ZnO</td>
<td>8.3x10^5</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>7.7x10^4</td>
</tr>
<tr>
<td>CdSnO$_2$</td>
<td>7.7x10^5</td>
</tr>
<tr>
<td>CdO:In</td>
<td>1.7x10^6</td>
</tr>
</tbody>
</table>

**ZnO:Al**
ZT~0.6 @ 1000 °C

**Fig. 10. TEM image of (Ti$_{0.3}$/Sn$_{0.7}$)$_2$O$_3$ ceramics annealed for 48 h.**
Shultz & Stubican, JACS, 53, 1970
Experimental

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

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 = αρC_p)

Seebeck/Resistivity

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

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**SnO₂ Sintering-Inhibited**

- Surface Diffusion <1100 °C
- Evaporation >1100 °C

SnO₂ → SnO + ½O₂(g)

**Sintering Aids-SnO₂**

- MnO, CoO, CuO, ZnO

CoO → Co⁺⁺⁺⁺ + V'O

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Ta₂O₅ & In₂O₃

Ineffective Sintering Aids

Ta₂O₅ → 2Ta⁺⁺⁺⁺₁,Sn + 2e⁻ + ½O₂

In₂O₃ → 2In⁺⁺⁺⁺₁,Sn + 2V'O
75/25 TiO₂/SnO₂

Undoped

1% Ta₂O₅

Large Grain

Small Grain

Nano-ppts

Diffuse Composition Fluctuation
• 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
  \( M_2O_5 = 2M_{Ti,Sn}^* + 2e^- + \frac{1}{2}O_2 + 4O^X_O \)

- No further σ increase above 2% dopant.

- In₂O₃, MnO & CoO – No σ increase

 Activation Energy

<table>
<thead>
<tr>
<th></th>
<th>0.97 ev</th>
<th>1% Nb₂O₅</th>
<th>0.25 ev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% Ta₂O₅</td>
<td>0.49 ev</td>
<td>4% Nb₂O₅</td>
<td>0.20 ev</td>
</tr>
<tr>
<td>1% Ta₂O₅</td>
<td>0.22 ev</td>
<td>1% In₂O₃</td>
<td>0.99 ev</td>
</tr>
<tr>
<td>2% Ta₂O₅</td>
<td>0.30 ev</td>
<td>1% CoO</td>
<td>1.6 ev</td>
</tr>
<tr>
<td>4% Ta₂O₅</td>
<td>0.26 ev</td>
<td>1% MnO</td>
<td>7.9 ev</td>
</tr>
</tbody>
</table>

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

σ to low

700 °C  500 °C  300 °C  100 °C

σ (S/m)

1000/T (K⁻¹)
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 \((\text{Ti}_x\text{Sn}_{1-x})\text{O}_{2-y}\) 
\[ (\text{Ti}_{0.5}\text{Sn}_{0.5})\text{O}_{2-y} \]

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

- $\text{H}_2$ Reduction
- $10^3$ to $10^4$ x

$$\sim 0$$ Seebeck Coefficient

• 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

4% Ta$_2$O$_5$-800 °C

\[ PF = S^2 \sigma \]
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

$(\text{Ti}_{0.75}\text{Sn}_{0.25})\text{O}_2-x$

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

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