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, TixSn$_{1-x}$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.
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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 (%)

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
- Low mass
- Oxidizing environment
- Low cost
Nanotechnology

Figure of Merit

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

- \( S \) - 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

Electronic 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>$\text{In}_2\text{O}_3$</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

$ZnO:Al$ $ZT \sim 0.6$ @ 1000 $^\circ$C

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

Seebeck/Resistivity

ΔT 0-50 °C/Furnace RT-1000 °C
Sintering

**SnO₂ Sintering-Inhibited**
- Surface Diffusion \(<1100 \, ^°C\)
- Evaporation \(>1100 \, ^°C\)

\[ \text{SnO}_2 \rightarrow \text{SnO} + \frac{1}{2}\text{O}_2(g) \]

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

\[ \text{CoO} \rightarrow \text{Co}_{Ti,Sn}'' + V_O^{**} \]

50/50 TiO₂/SnO₂

- **Sintering Controlled By SnO₂**
- Densification

75/25 TiO₂/SnO₂

- 1625 °C
- 1550 °C

50/50 TiO₂/SnO₂

- Phase Separation

Ta₂O₅ & In₂O₃

Ineffective Sintering Aids

\[ Ta_2O_5 \rightarrow 2Ta_{Ti,Sn}^* + 2e^- + \frac{1}{2}O_2 \]

\[ In_2O_3 \rightarrow 2In_{Ti,Sn}^* + 2V_O^* \]
75/25 TiO$_2$/SnO$_2$

Undoped

Large Grain

Small Grain

Nano-ppts

Diffuse Composition Fluctuation

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

Compositions

• 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

![Graph showing electrical conductivity vs. temperature for various dopants.]

- Ta₂O₅ & Nb₂O₅ - Increases σ
- M₂O₅ = 2M⁺Ti,Sn + 2e⁻ + ½O₂ + 4Oₐ
- 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>1% Ta₂O₅</th>
<th>2% Ta₂O₅</th>
<th>4% Ta₂O₅</th>
<th>1% In₂O₃</th>
<th>1% CoO</th>
<th>1% MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97 ev</td>
<td>1.25 ev</td>
<td>0.75 ev</td>
<td>0.49 ev</td>
<td>0.22 ev</td>
<td>0.30 ev</td>
<td>0.26 ev</td>
<td>0.99 ev</td>
<td>1.6 ev</td>
<td>7.9 ev</td>
</tr>
</tbody>
</table>

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

σ to low
• 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 \((Ti_xSn_{1-x})O_{2-y}\)

\((Ti_{0.5}Sn_{0.5})O_{2-y}\)

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

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

\(\sigma\) (S/m)

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

\(0.8\)

\(0.1\)

\(0.01\)

\(10\)

\(100\)

\(1000\)

\(10000\)

\(100000\)

\(1000000\)

\(700^\circ C\)

\(500^\circ C\)

\(300^\circ C\)

\(100^\circ C\)

Seebeck (\(\mu V/K\))

Temp. (\(^\circ C\))

H\(_2\) Reduction

10\(^3\) to 10\(^4\) x

\(-200\)

\(-400\)

\(-600\)

\(-800\)

\(-1000\)

\(-1200\)

\(-1400\)

\(100\)

\(200\)

\(300\)

\(400\)

\(500\)

\(600\)

\(700\)

\(800\)

\(900\)

\(1000\)

~0 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% Ta₂O₅-800 °C

Power Factor (µW/K²m)

Temp. (°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 ($\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% $\text{Nb}_2\text{O}_5$