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-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

Space Power Generation

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) at 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~0.6 @ 1000 °C

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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 ºC**
**Anneal 72 Hrs**

**Thermal Conductivity**
- Laser Flash Method - Thermal Diffusivity
- Standard
- Specific Heat - C_p - Laser Flash
- Thermal Conductivity (K = αρC_p)

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

ΔT 0-50 ºC/Furnace RT-1000 ºC
**Sintering**

50/50 TiO\textsubscript{2}/SnO\textsubscript{2}  
1625 °C

75/25 TiO\textsubscript{2}/SnO\textsubscript{2}  
1550 °C

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**SnO\textsubscript{2} Sintering-Inhibited**
- Surface Diffusion <1100 °C
- Evaporation >1100 °C

SnO\textsubscript{2} → SnO + \( \frac{1}{2} \)O\textsubscript{2}(g)

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**Sintering Aids-SnO\textsubscript{2}**
- MnO, CoO, CuO, ZnO

CoO → Co\textsubscript{Ti,Sn}'' + V\textsubscript{O}'''

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**Ta\textsubscript{2}O\textsubscript{5} & In\textsubscript{2}O\textsubscript{3}**
Ineffective Sintering Aids

\( Ta\textsubscript{2}O\textsubscript{5} \rightarrow 2Ta_{Ti,Sn}^\bullet + 2e^\bullet + \frac{1}{2}O\textsubscript{2} \)

\( In\textsubscript{2}O\textsubscript{3} \rightarrow 2In_{Ti,Sn}^\bullet + 2V\textsubscript{O}^\bullet \)
75/25 TiO$_2$/SnO$_2$

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

Sn rich
Ti rich
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
- No further σ increase above 2% dopant.
- In₂O₃, MnO & CoO – No σ increase

\[ M_2O_5 = 2M_{Ti,Sn}^* + 2e^- + \frac{1}{2}O_2 + 4O_O^X \]

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

σ to low

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>0.26 ev</td>
<td>0.97 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>
<td></td>
</tr>
</tbody>
</table>
Seebeck Coefficient
75/25 TiO$_2$/SnO$_2$

-400
-600
-800
-1000
-1200

100 200 300 400 500 600 700 800 900 1000

-1200

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

Seebeck (μV/K)

Temp. (°C)

TiO$_2$
• Undoped
• Reduced
• 1% Ta$_2$O$_5$
• 1% In$_2$O$_3$
• 1% CoO
• 1% MnO
• 0.5% Ta$_2$O$_5$
• 2% Ta$_2$O$_5$
• 4% Ta$_2$O$_5$
• 1% Nb$_2$O$_5$
• 4% Nb$_2$O$_5$
Semiconductor

• Improve electrical conductivity by forming oxygen deficient material (Ti\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2-y} 
  (Ti\textsubscript{0.5}Sn\textsubscript{0.5})O\textsubscript{2-y}

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

$\sigma$ (S/m) vs. $1/T$ (K\textsuperscript{-1})

H\textsubscript{2} Reduction $10^3$ to $10^4$ x

~0 Seebeck Coefficient

$\text{Seebeck (}\mu\text{V/K})$

Temp. (°C)
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% $\text{Ta}_2\text{O}_5$ produces the highest $\sigma$.
- Significant effect on low temperature $\sigma$.

$\sigma$ (S/m) vs. $1000/T$ (K$^{-1}$) for different concentrations of $\text{Ta}_2\text{O}_5$ and $\text{Nb}_2\text{O}_5$.