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 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 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

Specific Power (W/kg)

Conversion Efficiency (%)
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>$8 \times 10^5$</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 $^\circ$C

Fig. 10. TEM image of (Ti$_{0.5}$/Sn$_{0.5}$)O$_2$ 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

Seebeck/Resistivity
ZEM-3
6-22 mm
4-8 mm
ΔT 0-50 °C/Furnace RT-1000 °C

Thermal Conductivity

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

50/50 TiO₂/SnO₂

75/25 TiO₂/SnO₂

1625 °C

1550 °C

SnO₂ Sintering-Inhibited

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

SnO₂ → SnO + ½O₂(g)

Sintering Aids-SnO₂

• MnO, CoO, CuO, ZnO

CoO → Co⁹Ti,Sn + V⁹O

Ta₂O₅ & In₂O₃

Ineffective Sintering Aids

Ta₂O₅ → 2Ta°Ti,Sn + 2e° + ½O₂

In₂O₃ → 2In°Ti,Sn + 2VO°
75/25 TiO$_2$/SnO$_2$

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

- 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 TiO<sub>2</sub>/SnO<sub>2</sub>

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

\[ \frac{1000}{T} \text{ (K}^{-1}) \]

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

\[ \sigma \text{ to low} \]

- Ta<sub>2</sub>O<sub>5</sub> & Nb<sub>2</sub>O<sub>5</sub> - Increases \( \sigma \)

\[ M_2O_5 = 2M^{+}_{Ti,Sn} + 2e^- + \frac{1}{2}O_2 + 4O_X^0 \]

- No further \( \sigma \) increase above 2% dopant.

- In<sub>2</sub>O<sub>3</sub>, MnO & CoO – No \( \sigma \) increase

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.97 ev</td>
</tr>
<tr>
<td>1% Nb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.25 ev</td>
</tr>
<tr>
<td>0.5% Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.49 ev</td>
</tr>
<tr>
<td>4% Nb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.20 ev</td>
</tr>
<tr>
<td>1% Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.22 ev</td>
</tr>
<tr>
<td>1% In&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.99 ev</td>
</tr>
<tr>
<td>2% Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.30 ev</td>
</tr>
<tr>
<td>1% CoO</td>
<td>1.6 ev</td>
</tr>
<tr>
<td>4% Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.26 ev</td>
</tr>
<tr>
<td>1% MnO</td>
<td>7.9 ev</td>
</tr>
</tbody>
</table>
Seebeck Coefficient
75/25 TiO_2/SnO_2

-1200
-1000
-800
-600
-400

Seebeck (μV/K)

Temp. (°C)

• N-type
• Large Seebeck coefficients at low σ
• Increase Ta_2O_5 conc. reduces Seebeck coefficient
• Nb_2O_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?

H₂ Reduction 10³ to 10⁴ x

~0 Seebeck Coefficient

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

\[\frac{1}{T} \text{ (K⁻¹)}\]

Seebeck (μV/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% Ta₂O₅-800 °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

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

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