Nanotechnology has provided a new interest in thermoelectric technology. A thermodynamically driven process is one approach in achieving nanostructures in bulk materials. TiO2/SnO2 system exhibits a large spinodal region with exceptional stable phase separated microstructures up to 1400 °C. Fabricated TiO2/SnO2 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 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

<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>

**Electrical Conductivity**

**Coherent Nucleation & Growth**

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

ZnO:Al

$ZT \sim 0.6$ @ 1000 °C
**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**

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

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

50/50 TiO$_2$/SnO$_2$  
75/25 TiO$_2$/SnO$_2$

Sintering Controlled By SnO$_2$

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

SnO$_2$ $\rightarrow$ SnO + $\frac{1}{2}$O$_2$ (g)

**SnO$_2$ Sintering-Inhibited**

**SnO$_2$ Sintering Inhibited**

**Sintering Aids-SnO$_2$**

- MnO, CoO, CuO, ZnO

CoO $\rightarrow$ Co$_{Ti,Sn}''$ + $V_O^{**}$

Ta$_2$O$_5$ & In$_2$O$_3$

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

1% Ta$_2$O$_5$

Nano-ppts

Diffuse Composition Fluctuation

Sn rich

Ti rich
Thermal Conductivity

Compositions

- 1% MnO-50 TiO₂
- 1% CoO-50 TiO₂
- 1% MnO-75 TiO₂
- 1% CoO-75 TiO₂
- 1% MnO-25 TiO₂
- 1% CoO-25 TiO₂
- 1%Ta₂O₅/0.5% CoO-25 TiO₂

- Compositions exhibit low κ – 1.7 to 6.8 W/mK
- Observe no dependence on composition or post treatments
- Spinodal Decomposition – κ reduction?
- Best ZT ~ 0.05
### Electrical Conductivity

**75/25 TiO₂/SnO₂**

- **Activation Energy**
  - Undoped: 0.97 ev
  - 1% Nb₂O₅: 0.25 ev
  - 0.5% Ta₂O₅: 0.49 ev
  - 1% Ta₂O₅: 0.22 ev
  - 2% Ta₂O₅: 0.30 ev
  - 4% Ta₂O₅: 0.26 ev
  - 1% MnO: 7.9 ev

- **Ta₂O₅ & Nb₂O₅** - Increases $\sigma$
  \[
  M₂O₅ = 2M^{Si,Sn}_Ti + 2e^- + \frac{1}{2}O₂ + 4O^X_O
  \]

- No further $\sigma$ increase above 2% dopant.

- **In₂O₃, MnO & CoO** – No $\sigma$ increase

- **$ZT = \frac{S^2\sigma}{T\kappa}$**

**Graph:**
- TiO₂
- 0.5% Ta₂O₅
- 1% Ta₂O₅
- 2% Ta₂O₅
- 4% Ta₂O₅
- 1% Nb₂O₅
- Undoped

**Temperature (°C):**
- 700
- 500
- 300
- 100

**Conductivity (S/m):**
- 1000
- 100
- 10
- 1
- 0.1
- 0.01
- 0.001

**1000/T (K⁻¹):**
- 2.8
- 2.4
- 2.0
- 1.6
- 1.2
- 0.8

**σ** to low
Seebeck Coefficient
75/25 TiO₂/SnO₂

- TiO₂
- Undoped
- Reduced
- 1% Ta₂O₅
- 1% In₂O₃
- 1% CoO
- 1% MnO
- 0.5% Ta₂O₅
- 2% Ta₂O₅
- 4% Ta₂O₅
- 1% Nb₂O₅
- 4% Nb₂O₅

- N-type
- Large Seebeck coefficients at low σ
- Increase Ta₂O₅ conc. reduces Seebeck coefficient
- Nb₂O₅ doping most effective in Seebeck reduction
Semiconductor

• Improve electrical conductivity by forming oxygen deficient material \((Ti_xSn_{1-x})O_{2-y}\) \((Ti_{0.5}Sn_{0.5})O_{2-y}\)

\[\sigma (S/m)\]
\[1/T (K^{-1})\]

\[\text{Seebeck (}\mu\text{V/K)}\]
\[\text{Temp. (°C)}\]

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

• 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% 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**

\((Ti_{0.75}Sn_{0.25})O_{2-x}\)

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