Recent advances in improving efficiency of thermoelectric materials are linked to nanotechnology. Thermodynamically driven spinodal decomposition was utilized to synthesize bulk nanocomposites. TiO$_2$/SnO$_2$ system exhibits a large spinodal region, ranging from 15 to 85 mole % TiO$_2$. The phase separated microstructures are stable up to 1400 °C. Semiconducting TiO$_2$/SnO$_2$ powders were synthesized by solid state reaction between TiO$_2$ and SnO$_2$. High density samples were fabricated by pressureless sintering. Self assemble nanocomposites were achieved by annealing at 1000 to 1350 °C. X-ray diffraction reveal phase separation of (Ti$_x$Sn$_{1-x}$)O$_2$ type phases. The TiO$_2$/SnO$_2$ nanocomposites exhibit n-type behavior; a power factor of 70 W/mK$^2$ at 1000 °C has been achieved with penta-valent doping. Seebeck, thermal conductivity, electrical resistivity and microstructure will be discussed in relation to composition and doping.
Thermoelectric Properties of Self Assembled TiO$_2$/SnO$_2$ Nanocomposites

Fred Dynys, NASA-Glenn, USA
Ali Sayir, CWRU, USA
Alp Sehirlioglu, CWRU, USA

Program Support: NASA Radioisotope Power Systems
**Objective: High Conversion Efficiency**

- Reduces Mass, Volume & Cost

### Heat to Electric Power Generation

Voltage: n-type \( e^- \) \( e^- \) \( e^- \)

\( p^- \) \( h^+ \) \( h^+ \)

Load

- \( T_{hot} \)
- \( T_{cold} \)

- **ZTave~0.88**  \( \text{Zintl/Nano Si-Ge} \)
- **ZTave~0.75**  \( \text{Nano Si-Ge} \)
- **ZTave~0.55**  \( \text{RTG Si-Ge} \)
- **ZTave~1.1**  2x Improvement
- **ZTave~1.6**  3x Improvement

### Space Power Generation

- **Conversion Efficiency (%)**
- **Specific Power (W/kg)**

- **ZT~2.0**  \( \text{GPHS-RTG} \)
- **ZT~1.1**  2x Improvement
- **ZT~1.6**  3x Improvement
- **ZT~0.76**  \( \text{Nano Si-Ge} \)
- **ZT~0.88**  \( \text{Zintl/Nano Si-Ge} \)
- **ZT~0.55**  \( \text{RTG Si-Ge} \)

### Waste Heat to Power

- Waste Heat is one of our most under utilized energy resources
- U.S.-energy consumption \( \sim 29 \) tera-kWh \( (10^{12}) \)
  - Barrels of Oil – 170 giga-barrels \( (10^9) \)
- World-energy consumption \( \sim 120 \) tera- kWh \( (10^{12}) \)
- 20-65 percent is lost in the form of heat
- Maximizes efficiency
- Reduces CO\(_2\) emission
Figure of Merit

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

\( S \) - 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
• Supperlattices
• Alloying
• Crystal Structures
• Anharmonic vibrations
• Nano-technology

Fleurial/Chen – JPL/MIT
Fabrication of Nanostructure Solids

Goal: Preservation of the nanostructure during fabrication.

**Chen/MIT-κ Reduction**

1 nm Thick GB

Nano-powder Synthesis

**Thermal Densification**
Pressure Assisted
Microwave
Laser
Plasma-SPS/P²C

**Cold Densification**
Cold Spray
Dynamic Compaction
Plastic Deformation

**Post Process**

**Thermodynamics**
Phase Transformation
Precipitation
Spinodal Decomposition

Inhibit Grain Growth
•Rapid Thermal Process
•Inclusions

% Atoms in Grain Boundary

Alloy Limit

Microstructure Dependent on Thermal Aging
•Composition Limited

Si/Ge

1 nm Thick GB

K Reduction

www.nasa.gov
Spinodal Decomposition

**Desired Features**
- ~50 nm grains
- High Temperature
- Wide Composition
- Large $\Delta$ Mass

**Transparent Conducting Oxides**
- 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>$\text{In}_2\text{O}_3$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>$\text{SnO}_2$</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>$7.7 \times 10^4$</td>
</tr>
<tr>
<td>CdO:In</td>
<td>$1.7 \times 10^6$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

ZnO:Al $\text{ZT}=0.3$ @ 1000 °C

Fig. 10. TEM image of (Ti$_{0.5}$/Sn$_{0.5}$)O$_2$ ceramics annealed for 48 h.
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,MnO,
Ta₂O₅, In₂O₃

TiO₂/SnO₂
50/50 mol %
75/25 mol %
25/75 mol %

Powder Mixing
Compaction Die Press
Reactive Sintering
1250-1550 °C

Seebeck/Resistivity

Thermal Conductivity

- Laser Flash Method- Thermal Diffusivity
- Standard
- Specific Heat-Laser Flash
- Thermal Conductivity (K = αρCₚ)

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

Sintering-Controlled By SnO₂

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

SnO₂ → SnO + ½O₂(g)

**Sintering-Inhibited**

- 50/50 TiO₂/SnO₂
  - 1625 °C

- 75/25 TiO₂/SnO₂
  - 1550 °C

**50/50 TiO₂/SnO₂**

- Phase Separation

**Ta₂O₅ & In₂O₃**

- Ineffective Sintering Aids

  \[ Ta₂O₅ \rightarrow 2Ta^{\bullet}_{Ti,Sn} + 2e^{\bullet} + \frac{1}{2}O₂ \]

  \[ In₂O₃ \rightarrow 2In^{\bullet}_{Ti,Sn} + 2V_O^{\bullet} \]

**Sintering Aids**

- MnO, CoO, CuO, ZnO

  \[ CoO \rightarrow Co_{Ti,Sn}^{\bullet} + V_O^{\bullet} \]
75/25 TiO<sub>2</sub>/SnO<sub>2</sub>

1% Ta<sub>2</sub>O<sub>5</sub>

1% In<sub>2</sub>O<sub>3</sub>

XRD-Phases
Sintered – (Ti<sub>0.8</sub>Sn<sub>0.2</sub>)O<sub>2</sub>
Reduced – TiO<sub>2</sub>, Rutile
(Ti<sub>0.8</sub>Sn<sub>0.2</sub>)O<sub>2</sub>

1% Ta<sub>2</sub>O<sub>5</sub>

GB Phase

1% CoO XRD
Sintered – (Ti<sub>0.8</sub>Sn<sub>0.2</sub>)O<sub>2</sub>
(Ti<sub>0.2</sub>Sn<sub>0.8</sub>)O<sub>2</sub>
Annealed – (Ti<sub>0.9</sub>Sn<sub>0.1</sub>)O<sub>2</sub>
1000 °C (Ti<sub>0.1</sub>Sn<sub>0.9</sub>)O<sub>2</sub>

1% MnO XRD
Sintered – (Ti<sub>0.8</sub>Sn<sub>0.2</sub>)O<sub>2</sub>
(Ti<sub>0.2</sub>Sn<sub>0.8</sub>)O<sub>2</sub>
Annealed – (Ti<sub>0.9</sub>Sn<sub>0.1</sub>)O<sub>2</sub>
1000 °C (Ti<sub>0.1</sub>Sn<sub>0.9</sub>)O<sub>2</sub>

Phase Separation
50/50 TiO$_2$/SnO$_2$

XRD-Phases
- Sintered: (Ti$_{0.8}$Sn$_{0.2}$)O$_2$ (Ti$_{0.1}$Sn$_{0.9}$)O$_2$ (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
- Annealed: (Ti$_{0.8}$Sn$_{0.2}$)O$_2$ (Ti$_{0.1}$Sn$_{0.9}$)O$_2$

1% CoO

1% MnO

Microstructure Coarsening @ 1600 °C

Grain Boundary Phases Segregation
Electrical Conductivity

- Ta₂O₅ – Increases σ – $E_a \sim 0.25$ ev
- (TiₓSn₁₋ₓ)O₂₋ₚ – Oxygen Deficiency Increases σ – $E_a \sim 0.06$ ev
- Co-doping-Ta₂O₅/CoO - Increases σ – $E_a \sim 0.5-0.7$ ev
- In₂O₃, MnO & CoO – Ineffective in Enhancing σ – $E_a \sim 1-4.2$ ev
Seebeck Coefficient

- **N-type**
- Large Seebeck coefficients >-400 μV/K
- Large Seebeck coefficient – Low σ
- \((Ti_{0.5}Sn_{0.5})O_{2-y}\) low Seebeck ~ 0
• 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 $\sim 0.05$
In Summary

• TiO$_2$/SnO$_2$ compositions exhibit low thermal conductivity. Reduction in thermal conductance by spinodal microstructure has not been isolated.

• Improvements in electrical conductivity is needed. Grain boundary phases could be detrimental. Ta$_2$O$_5$ or oxygen deficiency enhances electrical conductivity.

• Sintering aids are required to densify equal-molar and tin oxide rich compositions. MnO and CoO promoted phase separation.