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

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Program Support: NASA Radioisotope Power Systems
Objective: High Conversion Efficiency
  ● Reduces Mass, Volume & Cost

Waste Heat to Power

- Waste Heat is one of our most under utilized energy resources
- 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
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
- 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

Nano-powder Synthesis

Inhibit Grain Growth
• Rapid Thermal Process
• Inclusions

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

• Microstructure Dependent on Thermal Aging
• Composition Limited

Si/Ge

Alloy Limit

1 nm Thick GB

% Atoms in Grain Boundary

Grain Size (nm)
Spinodal Decomposition

**Desired Features**
- ~50 nm grains
- High Temperature
- Wide Composition
- Large Δ 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>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>
<tr>
<td>TiO$_2$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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

Thermal Conductivity

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

Seebeck/Resistivity
-ZEM-3

6-22 mm

4-8 mm

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

50/50 TiO₂/SnO₂  75/25 TiO₂/SnO₂
1625 °C  1550 °C

Sintering Controlled By SnO₂

Sintering-Inhibited

• Surface Diffusion <1100 °C
• Evaporation >1100 °C
SnO₂ → SnO + ½O₂(g)

Sintering Aids

• MnO, CoO, CuO, ZnO

CoO → Co"ₜ₁,Sn + V"O

Ta₂O₅ & In₂O₃

Phase Separation

Ineffective Sintering Aids

Ta₂O₅ → 2Ta⁺ₜ₁,Sn + 2e⁻ + ½O₂

Ind₂O₃ → 2In⁺ₜ₁,Sn + 2Vₒ
**75/25 TiO₂/SnO₂**

**Undoped**

**1% Ta₂O₅**

**1% In₂O₃**

**XRD-Phases**

Sintered – (Ti₀.₈Sn₀.₂)O₂
Reduced – TiO₂, Rutile
(Ti₀.₈Sn₀.₂)O₂

**GB Phase**

**1% Ta₂O₅**

**XRD-Phases**

Sintered – (Ti₀.₈Sn₀.₂)O₂
Reduced – TiO₂, Rutile
(Ti₀.₈Sn₀.₂)O₂

**Annealed – TiO₂, Rutile**

SnO₂, In₂O₃

1250 °C

Reduced – TiO₂, Rutile
(Ti₀.₈Sn₀.₂)O₂

**1% MnO XRD**

Sintered – (Ti₀.₈Sn₀.₂)O₂
(Ti₀.₆Sn₀.₄)O₂

Annealed – (Ti₀.₉Sn₀.₁)O₂
1000 °C

(Ti₀.₉Sn₀.₁)O₂

1000 °C

Phase Separation
50/50 TiO₂/SnO₂

1% CoO

1% MnO

XRD-Phases
Sintered – (Ti₀.₈Sn₀.₂)O₂
(Ti₀.₂Sn₀.₈)O₂
TiO₂
Annealed – (Ti₀.₂Sn₀.₈)O₂
1000 °C  (Ti₀.₉Sn₀.₁)O₂

XRD-Phases
Sintered – (Ti₀.₈Sn₀.₂)O₂
(Ti₀.₁Sn₀.₉)O₂
Annealed – (Ti₀.₂Sn₀.₈)O₂
1000 °C  (Ti₀.₉Sn₀.₁)O₂

Grain Boundary Phases
Segregation

Microstructure
Coarsening
@ 1600 °C
Electrical Conductivity

- $\text{Ta}_2\text{O}_5$ – Increases $\sigma - E_a \approx 0.25$ ev
- $(\text{Ti}_x\text{Sn}_{1-x})\text{O}_{2-y}$ – Oxygen Deficiency Increases $\sigma - E_a \approx 0.06$ ev
- Co-doping-$\text{Ta}_2\text{O}_5$/CoO - Increases $\sigma - E_a \approx 0.5-0.7$ ev
- $\text{In}_2\text{O}_3$, MnO & CoO – Ineffective in Enhancing $\sigma - E_a \approx 1-4.2$ ev
Seebeck Coefficient

- **N-type**
- Large Seebeck coefficients >-400 μV/K
- Large Seebeck coefficient – Low σ
- 

\((\text{Ti}_{0.75}\text{Sn}_{0.25})\text{O}_{2-y}\) low Seebeck \(\sim 0\)
Thermal Conductivity

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$_2$

- 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.