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
Heat to Electric Power Generation

Objective: High Conversion Efficiency
- Reduces Mass, Volume & Cost

Space Power Generation

Waste Heat to Power

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

**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**

![Graph showing the figure of merit (ZT) over time, with different materials and years marked.](image-url)
Fabrication of Nanostructure Solids

Goal: Preservation of the nanostructure during fabrication.

Chen/MIT- κ Reduction

Nano-powder Synthesis

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

Cold Densification
- Cold Spray
- Dynamic Compaction
- Plastic Deformation

Post Process

Inhibit Grain Growth
- Rapid Thermal Process
- Inclusions

Thermodynamics
- Phase Transformation
- Precipitation
- Spinodal Decomposition

% Atoms in Grain Boundary

Si/Ge

Alloy Limit

1 nm Thick GB

• Microstructure Dependent on Thermal Aging
• Composition Limited
Spinodal Decomposition

**TiO\textsubscript{2} – SnO\textsubscript{2}**

**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>In\textsubscript{2}O\textsubscript{3}</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>SnO\textsubscript{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\textsubscript{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\textsubscript{2}</td>
<td>0.01</td>
</tr>
</tbody>
</table>

ZnO:Al
ZT=0.3 @ 1000 oC

**Fig. 10.** TEM image of (Ti$_{0.5}$/Sn$_{0.5}$)$_2$O$_3$ ceramics annealed for 48 h.
SnO₂
Purity: 99.9%
APS: 50 nm
SSA: 14.2 m²/g

TiO₂
Purity: 99.99 %
APS: 20 nm,
SSA: > 30 m²/g

Dopants
CoO, MnO
Ta₂O₅, In₂O₃

Experimental

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 = αρC_p)

Seebeck/Resistivity

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

Sintering-Controlled By SnO₂

Sintering-Inhibited
- Surface Diffusion <1100 °C
- Evaporation >1100 °C
SnO₂ → SnO + ½O₂\text{(g)}

Sintering Aids
- MnO, CoO, CuO, ZnO

CoO → Co_{\text{Ti,Sn}}^{\text{"}} + V_O^{\text{"}}

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids

Ta₂O₅ → 2Ta_{\text{Ti,Sn}}^{\text{\bullet}} + 2e^{\text{\bullet}} + \frac{1}{2}O₂

In₂O₃ → 2In_{\text{Ti,Sn}}^{\prime} + 2V_O^{\text{\bullet}}

50/50 TiO₂/SnO₂

75/25 TiO₂/SnO₂

50/50 TiO₂/SnO₂

1625 °C

1550 °C

50/50 TiO₂/SnO₂

Phase Separation
75/25 TiO$_2$/SnO$_2$

**Undoped**

- **XRD-Phases**
  - Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
  - Reduced – TiO$_2$, Rutile
    (Ti$_{0.8}$Sn$_{0.2}$)O$_2$

- **1% Ta$_2$O$_5**
  - GB Phase

- **1% In$_2$O$_3**

**Annealed –**

- Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
- Annealed – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
  - 1250 °C
- Reduced – TiO$_2$, Rutile
  (Ti$_{0.8}$Sn$_{0.2}$)O$_2$

- SnO$_2$, In$_2$O$_3$

**Reduced –**

- TiO$_2$, Rutile

**Phase Separation**

**1% Ta$_2$O$_5$ XRD**

- Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
- Annealed – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
  - 1000 °C
- Reduced – (Ti$_{0.1}$Sn$_{0.9}$)O$_2$

**1% CoO XRD**

- Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
- Annealed – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
  - 1000 °C
- 1% CoO

**1% MnO XRD**

- Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
- Annealed – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
  - 1000 °C
- 1% MnO
50/50 TiO$_2$/SnO$_2$

1% CoO

1% MnO

XRD-Phases
Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
(Ti$_{0.2}$Sn$_{0.8}$)O$_2$
TiO$_2$
Annealed – (Ti$_{0.2}$Sn$_{0.8}$)O$_2$
1000 °C (Ti$_{0.9}$Sn$_{0.1}$)O$_2$

XRD-Phases
Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
(Ti$_{0.1}$Sn$_{0.9}$)O$_2$
Annealed – (Ti$_{0.2}$Sn$_{0.8}$)O$_2$
1000 °C (Ti$_{0.9}$Sn$_{0.1}$)O$_2$

Microstructure
Coarsening @ 1600 °C

Grain Boundary Phases
Segregation
Electrical Conductivity

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

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

1% Ta$_2$O$_5$

(Ti$_{0.75}$Sn$_{0.25}$)O$_{2-y}$

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

(Ti$_{0.5}$Sn$_{0.5}$)O$_{2-y}$

• 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 ~ 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.