Thermoelectric Properties of Self Assembled TiO$_2$/SnO$_2$ Nanocomposites

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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.
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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 ~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

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

- **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

![Graphs showing figure of merit over time with specific materials and year comparisons](image)

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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

Alloy Limit

Si/Ge

% Atoms in Grain Boundary

Grain Size (nm)

0 10 20 30 40 50 60 70 80 90 100

0 10 20 30 40 50 60 70 80 90 100

• Microstructure Dependent on Thermal Aging
• Composition Limited
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>8x10^5</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>1x10^6</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>2.5x10^5</td>
</tr>
<tr>
<td>ZnO</td>
<td>8.3x10^5</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>7.7x10^4</td>
</tr>
<tr>
<td>CdSnO$_2$</td>
<td>7.7x10^4</td>
</tr>
<tr>
<td>CdO:In</td>
<td>1.7x10^6</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

ZnO:Al
$ZT=0.3$ @ 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

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

Sintering Controlled By SnO₂

Densification

Sintering-Inhibited

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

SnO₂ → SnO + ½O₂(g)

Sintering Aids

- MnO, CoO, CuO, ZnO

CoO → Co⁰⁺₁ₓ,TiSn + V⁰⁺₀

50/50 TiO₂/SnO₂

1625 °C

75/25 TiO₂/SnO₂

1550 °C

Ta₂O₅ & In₂O₃

Ineffective Sintering Aids

Ta₂O₅ → 2Ta⁺¹,Tiₐ,Sn + 2e⁻ + ½O₂

In₂O₃ → 2In⁺¹,Tiₐ,Sn + 2V⁰⁺₀
75/25 TiO$_2$/SnO$_2$

**Undoped**

**XRD-Phases**

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

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

**XRD-Phases**

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

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

**XRD-Phases**

- **Sintered** – TiO$_2$, Rutile
  - SnO$_2$, In$_2$O$_3$
- **Annealed** – TiO$_2$, Rutile
  - SnO$_2$, In$_2$O$_3$

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

**GB Phase**

**1% CoO XRD**

- **Sintered** – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
  - (Ti$_{0.2}$Sn$_{0.8}$)O$_2$
- **Annealed** – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
  - (Ti$_{0.1}$Sn$_{0.9}$)O$_2$

**1% MnO XRD**

- **Sintered** – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
  - (Ti$_{0.2}$Sn$_{0.8}$)O$_2$
- **Annealed** – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
  - (Ti$_{0.1}$Sn$_{0.9}$)O$_2$
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 $\sigma$ – $E_a\sim0.25$ ev
• $(\text{Ti}_x\text{Sn}_{1-x})\text{O}_{2-y}$ – Oxygen Deficiency Increases $\sigma$ – $E_a\sim0.06$ ev
• Co-doping-$\text{Ta}_2\text{O}_5$/CoO - Increases $\sigma$ – $E_a\sim0.5$-0.7 ev
• $\text{In}_2\text{O}_3$, MnO & CoO – Ineffective in Enhancing $\sigma$ – $E_a\sim1$-4.2 ev
Seebeck Coefficient

- **N-type**
- Large Seebeck coefficients >-400 $\mu$V/K
- Large Seebeck coefficient – Low $\sigma$
- $(Ti_{0.75}Sn_{0.25})O_{2-y}$ low Seebeck $\sim 0$
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 $\kappa$ – 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.