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

Heat to Electric Power Generation

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**

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

- $S$ - Seebeck coefficient
- $\sigma$ – electrical conductivity
- $\kappa$ – thermal conductivity

**Efficiency**

$$\eta_{\text{max}} = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1 + ZT}}{\sqrt{1 + ZT} + \frac{T_{\text{cold}}}{T_{\text{hot}}}}$$

**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- $\kappa$ Reduction

Nano-powder Synthesis

Thermal Densification
Pressure Assisted
Microwave
Laser
Plasma-SPS/P²C

Cold Densification
Cold Spray
Dynamic Compaction
Plastic Deformation

Inhibit Grain Growth
• Rapid Thermal Process
• Inclusions

Post Process

Thermodynamics
Phase Transformation
Precipitation
Spinodal Decomposition

1 nm Thick GB

% Atoms in Grain Boundary

Alloy Limit

Si/Ge

Grain Size (nm)

$\kappa$ Reduction

• Microstructure
  Dependent on Thermal Aging
  • Composition Limited
Spinodal Decomposition

**desired Features**
- \(\approx 50\) 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>(\text{ZnO})</td>
<td>(8.3 \times 10^5)</td>
</tr>
<tr>
<td>(\text{ZnO:Al})</td>
<td>(7.7 \times 10^4)</td>
</tr>
<tr>
<td>(\text{CdSnO}_2)</td>
<td>(7.7 \times 10^5)</td>
</tr>
<tr>
<td>(\text{CdO:In})</td>
<td>(1.7 \times 10^6)</td>
</tr>
<tr>
<td>(\text{TiO}_2)</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(\text{ZnO:Al}\) \(ZT=0.3\) @ 1000 °C

Fig. 10. TEM image of \((\text{Ti}_0.5/\text{Sn}_0.5)\text{O}_2\) ceramics annealed for 48 h.
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 = αρ Cv)

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(g)

**Sintering Aids**
- MnO, CoO, CuO, ZnO

CoO → Co"Ti,Sn + V'O

**50/50 TiO₂/SnO₂**

1625 °C

**75/25 TiO₂/SnO₂**

1550 °C

Ta₂O₅ & In₂O₃

Ineffective Sintering Aids

Ta₂O₅ → 2Ta"Ti,Sn + 2e' + ½O₂

In₂O₃ → 2In'Ti,Sn + 2V'O
**75/25 TiO<sub>2</sub>/SnO<sub>2</sub>**

**Undoped**

**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>**

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

**XRD-Phases**
- Sintered – TiO<sub>2</sub>, Rutile
- SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>
- Annealed – TiO<sub>2</sub>, Rutile
- SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</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>
- (Ti<sub>0.1</sub>Sn<sub>0.9</sub>)O<sub>2</sub>

**1000 °C**

**Phase Separation**

**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>
- (Ti<sub>0.1</sub>Sn<sub>0.9</sub>)O<sub>2</sub>
50/50 TiO$_2$/SnO$_2$

1% CoO

1% MnO

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

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

Microstructure Coarsening @ 1600 \degree \text{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
• 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
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.