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 CO\(_2\) emission
Nanotechnology

Figure of Merit

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

- \( S \): Seebeck coefficient
- \( \sigma \): Electrical conductivity
- \( \kappa \): Thermal conductivity

Efficiency

\[ \eta_{\text{max}} = \frac{\Delta T}{T_{\text{hot}}} \left( \sqrt{1 + ZT} - 1 \right) \]

- \( \Delta T \): Temperature difference
- \( T_{\text{hot}} \): Hot temperature
- \( T_{\text{cold}} \): Cold temperature

Phonon Scattering:
- Atom disorder
- Supperlattices
- Alloying
- Crystal structures
- Anharmonic vibrations
- Nano-technology

Fleurial/Chen – JPL/MIT

Graphs showing the evolution of figure of merit (ZT) from 1940 to 2020 for various materials and alloys.
Fabrication of Nanostructure Solids
Goal: Preservation of the nanostructure during fabrication.

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

Microstructure
- Dependent on Thermal Aging
- Composition Limited

Si/Ge

Alloy Limit

1 nm Thick GB

% Atoms in Grain Boundary vs. 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>σ(S/m) @ RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>8x10⁵</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>1x10⁶</td>
</tr>
<tr>
<td>SnO₂</td>
<td>2.5x10⁵</td>
</tr>
<tr>
<td>ZnO</td>
<td>8.3x10⁵</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>7.7x10⁴</td>
</tr>
<tr>
<td>CdSnO₂</td>
<td>7.7x10⁴</td>
</tr>
<tr>
<td>CdO:In</td>
<td>1.7x10⁶</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
</tr>
</tbody>
</table>

ZnO:Al
ZT=0.3 @ 1000 °C

Fig. 10. TEM image of (Ti₅/₃Sn₄/₃)O₂ 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

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 = αρCₚ)

Seebeck/Resistivity
ZEM-3
6-22 mm
4-8 mm

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 TiO₂/SnO₂**

**Undoped**

**XRD-Phases**
- Sintered – (Ti₀.₈Sn₀.₂)O₂
- Reduced – TiO₂, Rutile
- (Ti₀.₈Sn₀.₂)O₂

**1% Ta₂O₅**

**XRD-Phases**
- Sintered – (Ti₀.₈Sn₀.₂)O₂
- Annealed – (Ti₀.₈Sn₀.₂)O₂
- 1250 °C
- Reduced – TiO₂, Rutile
- (Ti₀.₈Sn₀.₂)O₂

**1% In₂O₃**

**XRD-Phases**
- Sintered – TiO₂, Rutile
- SnO₂, In₂O₃
- Annealed – TiO₂, Rutile
- 1250 °C
- SnO₂, In₂O₃

**Phase Separation**

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

**1% MnO XRD**
- Sintered – (Ti₀.₈Sn₀.₂)O₂
- (Ti₀.₂Sn₀.₈)O₂
- Annealed – (Ti₀.₉Sn₀.₁)O₂
- 1000 °C
- (Ti₀.₁Sn₀.₉)O₂
50/50 TiO<sub>2</sub>/SnO<sub>2</sub>

1% CoO

1% MnO

XRD-Phases
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>
TiO<sub>2</sub>
Annealed – (Ti<sub>0.2</sub>Sn<sub>0.8</sub>)O<sub>2</sub>
1000 °C  (Ti<sub>0.9</sub>Sn<sub>0.1</sub>)O<sub>2</sub>

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

Microstructure
Coarsening @ 1600 °C

Grain Boundary Phases
Segregation
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
- \((\text{Ti}_{0.5}\text{Sn}_{0.5})\text{O}_{2-y}\) low Seebeck ~ 0

**75/25 TiO₂/SnO₂**

- TiO₂
- Undoped
- 1% Ta₂O₅
- 1% In₂O₃
- 1% CoO
- 1% MnO

**50/50 & 25/75 TiO₂/SnO₂**

- 1% Ta₂O₅/0.5% CoO
- \((\text{Ti}_{0.5}\text{Sn}_{0.5})\text{O}_{2-y}\)
**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 $\sim$ 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.