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

Fred Dynys*, NASA Glenn, USA;
Ali Sayir, Alp Sehirlioglu, Case Western Reserve University, USA

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

Fred Dynys, NASA-Glenn, USA
Ali Sayir, CWRU, USA
Alp Sehirlioglu, CWRU, USA

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

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

\( S \) - 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**

Si/Ge

**Nanopowder 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

- Microstructure Dependent on Thermal Aging
- Composition Limited

Inhibit Grain Growth
- Rapid Thermal Process
- Inclusions

1 nm Thick GB

Alloy Limit

% Atoms in Grain Boundary

Thermal Conductivity (W/mK)

Interface Area/Volume (nm⁻¹)

% Atoms in Grain Boundary

Grain Size (nm)
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>$8 \times 10^5$</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>

**ZnO:Al**

ZT=0.3 @ 1000 °C
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-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

75/25 TiO₂/SnO₂

Ta₂O₅ & In₂O₃

Ineffective Sintering Aids

Ta₂O₅ → 2Ta^{'}_{Ti,Sn} + 2e^{'} + ½O₂

In₂O₃ → 2In^{'}_{Ti,Sn} + 2V_O^{*}
**75/25 TiO₂/SnO₂**

- **Undoped**
- **1% Ta₂O₅**
- **1% In₂O₃**

**XRD-Phases**

- **Sintered** – \((\text{Ti}_{0.8}\text{Sn}_{0.2})\text{O}_2\)
- **Reduced** – TiO₂, Rutile
- **(Ti_{0.8}\text{Sn}_{0.2})\text{O}_2**

**Annealed** – \((\text{Ti}_{0.8}\text{Sn}_{0.2})\text{O}_2\)

- **1250 °C**
- **SnO₂, In₂O₃**

**GB Phase**

- **1% Ta₂O₅**

**Phase Separation**

**1% CoO XRD**

- **Sintered** – \((\text{Ti}_{0.8}\text{Sn}_{0.2})\text{O}_2\)
- **Annealed** – \((\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_2\)
- **1000 °C**
- **(Ti_{0.1}\text{Sn}_{0.9})\text{O}_2**

**1% MnO XRD**

- **Sintered** – \((\text{Ti}_{0.8}\text{Sn}_{0.2})\text{O}_2\)
- **Annealed** – \((\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_2\)
- **1000 °C**
- **(Ti_{0.1}\text{Sn}_{0.9})\text{O}_2**
**50/50 TiO₂/SnO₂**

**XRD-Phases**

Sintered – (Ti_{0.8}Sn_{0.2})O₂

(Ti_{0.2}Sn_{0.8})O₂,

TiO₂

Annealed – (Ti_{0.2}Sn_{0.8})O₂

1000 °C  (Ti_{0.9}Sn_{0.1})O₂

**Microstructure Coarsening @ 1600 °C**

**XRD-Phases**

Sintered – (Ti_{0.8}Sn_{0.2})O₂

(Ti_{0.1}Sn_{0.9})O₂

Annealed – (Ti_{0.2}Sn_{0.8})O₂

1000 °C  (Ti_{0.9}Sn_{0.1})O₂

**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

- N-type
- Large Seebeck coefficients >-400 $\mu$V/K
- Large Seebeck coefficient – Low $\sigma$
- $(\text{Ti}_{0.5}\text{Sn}_{0.5})\text{O}_{2-y}$ low Seebeck $\sim 0$
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 $\sim$ 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.