Thermoelectric Properties of Self Assemble 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$_{1-x}$)$_2$O$_2$ type phases. The TiO$_2$/SnO$_2$ nanocomposites exhibit n-type behavior; a power factor of 70 μW/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

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

Phonon Scattering:

- Atom disorder
- Supperlattices
- Alloying
- Crystal Structures
- Anharmonic vibrations
- Nano-technology

Fleurial/Chen – JPL/MIT

Si/Ge

Alloy Limit
Fabrication of Nanostructure Solids

Goal: Preservation of the nanostructure during fabrication.

- **Nano-powder Synthesis**
- **Nano-Powder**

**Traditional**

- **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
- Lower Temperature

**New Approach**

- **Grain Size**
  - Thermal Aging
  - Composition Limited
  - Stable
Spinodal Decomposition

**Desired Features**
- ~50 nm grains
- High Temperature
- Wide Composition
- Large Δ Mass

**Transparent Conducting Oxides**
**Insulator/Semiconductor/Conductor**
- 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>7.7x10^5</td>
</tr>
<tr>
<td>CdO:In</td>
<td>1.7x10^6</td>
</tr>
</tbody>
</table>

**ZnO:Al**
ZT~0.6 @ 1000 °C

**Fig. 10. TEM image of (Ti,Sn)/Sn\(_2\)O\(_3\))O\(_2\) ceramics annealed for 48 h.**
Shultz & Stubican, JACS, 53, 1970
**Experimental**

<table>
<thead>
<tr>
<th>SnO₂</th>
<th>TiO₂ Rutile</th>
<th>Dopants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity: 99.9%</td>
<td>Purity: 99.99%</td>
<td>CoO, MnO₂, Ta₂O₅, In₂O₃</td>
</tr>
<tr>
<td>APS: 50 nm</td>
<td>APS: 20 nm, SSA: &gt; 30 m²/g</td>
<td></td>
</tr>
<tr>
<td>SSA: 14.2 m²/g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Dopants**

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**Temperature Ranges**

- ΔT 0-50 °C/Furnace RT-1000 °C

**Dopants**

| CoO, MnO₂, Ta₂O₅, In₂O₃ |

**Preparation Steps**

- **TiO₂/SnO₂**
  - 50/50 mol %
  - 75/25 mol %
  - 25/75 mol %
- Powder Mixing
- Compaction
- Reactive Sintering 1250-1550 °C
- Anneal 72 Hrs

**Thermal Conductivity**

- Laser Flash Method - Thermal Diffusivity
- Standard
- Specific Heat - Cₚ - Laser Flash
- Thermal Conductivity (K = αρCₚ)

**Seebeck/Resistivity**

- ZEM-3
- 6-22 mm
- 4-8 mm

www.nasa.gov  6
**Sintering**

**SnO₂ Sintering-Inhibited**
- Surface Diffusion $<$1100 °C
- Evaporation $>$1100 °C

$\text{SnO}_2 \rightarrow \text{SnO} + \frac{1}{2}\text{O}_2(g)$

**Sintering Aids-SnO₂**
- MnO, CoO, CuO, ZnO

$\text{CoO} \rightarrow \text{Co}_{\text{Ti,Sn}} + V_{\text{O}}^{\text{Ti,Sn}}$

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**TiO₂/SnO₂**

**50/50 TiO₂/SnO₂**

1625 °C

**75/25 TiO₂/SnO₂**

1550 °C

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**Ta₂O₅ & In₂O₃**

Ineffective Sintering Aids

$\text{Ta}_2\text{O}_5 \rightarrow 2\text{Ta}^{\text{Ti,Sn}}_\text{Ti,Sn} + 2e^- + \frac{1}{2}\text{O}_2$

$\text{In}_2\text{O}_3 \rightarrow 2\text{In}^{\text{Ti,Sn}}_\text{Ti,Sn} + 2V_{\text{O}}^*$
75/25 TiO$_2$/SnO$_2$

Undoped

1% Ta$_2$O$_5$

1% In$_2$O$_3$

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

XRD-Phases
Sintered – TiO$_2$, Rutile
SnO$_2$, In$_2$O$_3$
Annealed – TiO$_2$, Rutile
1250 °C
SnO$_2$, In$_2$O$_3$

XRD-Phases
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$_2$

GB Phase

1% Ta$_2$O$_5$

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$_2$
1000 °C
(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$_2$
1000 °C
(Ti$_{0.1}$Sn$_{0.9}$)O$_2$

Phase Separation
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$_2$

**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
- In$_2$O$_3$, MnO & CoO – Ineffective in Enhancing $\sigma$ – $E_a \sim 1-4.2$ ev
Seebeck Coefficient

75/25 TiO₂/SnO₂

- N-type
- Large Seebeck coefficients >-400 μV/K
- Large Seebeck coefficient – Low σ
- (Ti₀.₇₅Sn₀.₂₅)O₂₋ᵧ low Seebeck ~ 0
Thermal Conductivity

Compositions

- 1% MnO-50 TiO$_2$
- 1% CoO-50 TiO$_2$
- 1% MnO-75 TiO$_2$
- 1% CoO-75 TiO$_2$
- 1% MnO-25 TiO$_2$
- 1% CoO-25 TiO$_2$
- 1%Ta$_2$O$_5$/0.5% CoO-25 TiO$_2$

- 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.