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

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**Space Power Generation**

- **ZTave~0.75**
  - Zintl/Nano Si-Ge
- **ZTave~0.55**
  - RTG Si-Ge
- **ZTave~1.1**
  - 2x Improvement
- **ZTave~1.6**
  - 3x Improvement

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**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

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**Specific Power (W/kg) vs. Conversion Efficiency (%)**

- ZTave~0.75 Nano Si-Ge
- ZTave~0.55 RTG Si-Ge
- ZTave~1.1 2x Improvement
- ZTave~1.6 3x Improvement

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**Voltage**

- n-type
  - $e^-$
- p-type
  - $h^+$

**Load**

- **$T_{hot}$**
- **$T_{cold}$**

**Thermal Power Plant**

- Carnot Cycle
- Thermionic Generators
- Stirling Generator
- Automotiv e Engines
- Diesel

**Temperature Ratio ($T_{hot} / T_{cold}$)**

- 0.5
- 0.6
- 0.7
- 0.8
- 0.9
- 1.0

**Power Generation Efficiency**

- **Thermoelectric Power Generators**
- **Thermionic Generators**
- **Stirling Generator**
- **Automotive Engines**
- **Diesel**
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
- Alloying
- Anharmonic vibrations

Fleurial/Chen – JPL/MIT
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

Post Process

Thermodynamics
- Phase Transformation
- Precipitation
- Spinodal Decomposition

Inhibit Grain Growth
- Rapid Thermal Process
- Inclusions

Chen/MIT- $\kappa$ Reduction

Si/Ge

Alloy Limit

$\kappa$ Reduction

1 nm Thick GB

% Atoms in Grain Boundary

Grain Size (nm)

- 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>$8 \times 10^5$</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

ΔT 0-50 °C/Furnace RT-1000 °C
Sintering

50/50 TiO₂/SnO₂
1625 °C

75/25 TiO₂/SnO₂
1550 °C

Sintering-Inhibited
• Surface Diffusion <1100 °C
• Evaporation >1100 °C
SnO₂ → SnO + 1/2O₂(g)

Sintering Aids
• MnO, CoO, CuO, ZnO

CoO → Co⁹⁺<sub>Ti,Sn</sub> + V<sub>O</sub>⁹⁺

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids

Ta₂O₅ → 2Ta⁹⁺<sub>Ti,Sn</sub> + 2e⁻ + 1/2O₂

In₂O₃ → 2In⁹⁺<sub>Ti,Sn</sub> + 2V<sub>O</sub>⁻
**75/25 TiO₂/SnO₂**

### 1% Ta₂O₅
- **Sintered** - (Ti₀.₈Sn₀.₂)O₂
- **Reduced** - TiO₂, Rutile (Ti₀.₈Sn₀.₂)O₂

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

### GB Phase

### 1% In₂O₃
- **Annealed** - TiO₂, Rutile SnO₂, In₂O₃

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

### Phase Separation

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

### 1% MnO XRD
- **Sintered** - (Ti₀.₈Sn₀.₂)O₂ (Ti₀.₂Sn₀.₈)O₂
- **Annealed** - (Ti₀.₉Sn₀.₁)O₂ (Ti₀.₁Sn₀.₉)O₂
  - 1000 °C
50/50 TiO$_2$/SnO$_2$

**XRD-Phases**

**Sintered** – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
(Ti$_{0.2}$Sn$_{0.8}$)O$_2$

**Annealed** – (Ti$_{0.2}$Sn$_{0.8}$)O$_2$
1000 °C (Ti$_{0.9}$Sn$_{0.1}$)O$_2$

**1% CoO**

**1% MnO**

**Microstructure Coarsening @ 1600 °C**

**Grain Boundary Phases Segregation**
### Electrical Conductivity

- **Ta_2O_5** – Increases $\sigma$ – $E_a \sim 0.25$ ev
- $(Ti_x Sn_{1-x})O_{2-y}$ – Oxygen Deficiency Increases $\sigma$ – $E_a \sim 0.06$ ev
- Co-doping-Ta_2O_5/CoO - Increases $\sigma$ – $E_a \sim 0.5-0.7$ ev
- In_2O_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 $\sigma$**
- $(Ti_{0.5}Sn_{0.5})O_{2-y}$ low Seebeck $\sim 0$
Thermal Conductivity

- 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

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- 25TiO$_2$
- 1%Ta$_2$O$_5$/0.5% CoO-25 TiO$_2$
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.