Thermoelectric Properties of Self Assemble 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$_{1-x}$)$_2$O$_5$ 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

![Diagram of Heat to Electric Power Generation](image-url)

![Diagram of Waste Heat to Power](image-url)
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.

Inhibit Grain Growth
• Rapid Thermal Process
• Inclusions
• Lower Temperature

Thermal Densification
- Pressure Assisted
- Microwave
- Laser
- Plasma-SPS/P²C

Cold Densification
- Cold Spray
- Dynamic Compaction
- Plastic Deformation

Thermodynamics
- Phase Transformation
- Precipitation
- Spinodal Decomposition

Nano-powder Synthesis

Nano-Powder

Post Process

New Approach

Grain Size
• Thermal Aging
• Composition Limited
• Stable

Traditional
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>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>
</tbody>
</table>

ZnO:Al
ZT ~0.6 @ 1000°C

Fig. 10. TEM image of (Ti\(_0.5\)/Sn\(_0.5\))O\(_2\) ceramics annealed for 48 h.
Shultz & stubican, JACS, 53, 1970
Experimental

- **SnO$_2$**
  - Purity: 99.9%
  - APS: 50 nm
  - SSA: 14.2 m$^2$/g

- **TiO$_2$ Rutile**
  - Purity: 99.99%
  - APS: 20 nm, SSA: > 30 m$^2$/g

- **Dopants**
  - CoO, MnO$_2$
  - Ta$_2$O$_5$, In$_2$O$_3$

**TiO$_2$/SnO$_2$**
- 50/50 mol %
- 75/25 mol %
- 25/75 mol %

- **Powder Mixing**
- **Compaction Die Press**
- **Reactive Sintering** 1250-1550 ºC
- **Anneal** 72 Hrs

**Thermal Conductivity**
- Laser Flash Method - Thermal Diffusivity
- Standard
- Specific Heat - $C_p$ - Laser Flash
- Thermal Conductivity ($K = \alpha \rho C_p$)

**Seebeck/Resistivity**
- ΔT 0-50 ºC/Furnace RT-1000 ºC
- ZEM-3
- 6-22 mm
- 4-8 mm
Sintering

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

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

CoO → Coₜ𝑖,𝑠𝑛 + V₀²⁺

50/50 TiO₂/SnO₂

1625 °C

75/25 TiO₂/SnO₂

1550 °C

Phase Separation

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids

Ta₂O₅ → 2Taₜ𝑖,𝑠𝑛 + 2e⁻ + 1/2O₂

In₂O₃ → 2Inₜ𝑖,𝑠𝑛 + 2V₀
**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% Ta₂O₅**

**GB Phase**

**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 TiO₂/SnO₂

1% CoO

1% MnO

XRD-Phases
Sintered – (Ti₀.₈Sn₀.₂)O₂
(Ti₀.₂Sn₀.₈)O₂
TiO₂
Annealed – (Ti₀.₂Sn₀.₈)O₂
1000 °C (Ti₀.₉Sn₀.₁)O₂

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

Microstructure
Coarsening
@ 1600 °C

Grain Boundary Phases
Segregation
Electrical Conductivity

75/25 TiO₂/SnO₂

50/50 & 25/75 TiO₂/SnO₂

- Ta₂O₅ – Increases σ – Eₐ~0.25 eV
- (TiₓSn₁₋ₓ)O₂₋ₘ – Oxygen Deficiency Increases σ – Eₐ~0.06 eV
- Co-doping-Ta₂O₅/CoO - Increases σ – Eₐ~0.5-0.7 eV
- In₂O₃, MnO & CoO – Ineffective in Enhancing σ – Eₐ~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 $\sim 0$

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**Graphs showing**

75/25 TiO$_2$/SnO$_2$

50/50 & 25/75 TiO$_2$/SnO$_2$
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. |