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$_{1-x}$)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 CO₂ emission
Nanotechnology

Figure of Merit

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

- S - Seebeck coefficient
- \( \sigma \) – electrical conductivity
- \( \kappa \) – thermal conductivity

Efficiency

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

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

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

New Approach
Grain Size
- Thermal Aging
- Composition Limited
- Stable

Post Process

Thermodynamics
Phase Transformation
Precipitation
Spinodal Decomposition

Cold Densification
Cold Spray
Dynamic Compaction
Plastic Deformation

Thermal Densification
Pressure Assisted
Microwave
Laser
Plasma-SPS/P²C

Traditional

Nano-powder Synthesis

Nano-Powder
Spinodal Decomposition

Desired Features
- ~50 nm grains
- High Temperature
- Wide Composition
- Large $\Delta$ 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
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, MnO₂
Ta₂O₅, In₂O₃

TiO₂/SnO₂
50/50 mol %
75/25 mol %
25/75 mol %

Powder Mixing
Compaction Die Press

Reactive Sintering
1250-1550 °C

Anneal
72 Hrs

Thermal Conductivity

- Laser Flash Method - Thermal Diffusivity
- Standard
- Specific Heat - C_p - Laser Flash
- Thermal Conductivity (K = αρC_p)

Seebeck/Resistivity

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

SnO₂ Sintering-Inhibited
- Surface Diffusion <1100 °C
- Evaporation >1100 °C
SnO₂ →SnO + ½O₂(g)

Sintering Aids-SnO₂
- MnO, CoO, CuO, ZnO
CoO → Co⁹°₉,Ti,Sn + V⁰°O

50/50 TiO₂/SnO₂
- 1625 °C

75/25 TiO₂/SnO₂
- 1550 °C

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids
Ta₂O₅ → 2Ta⁹°₉,Ti,Sn + 2e° + ½O₂
In₂O₃ → 2In⁹°₉₉,Ti,Sn + 2V°O
75/25 TiO$_2$/SnO$_2$

**Undoped**

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

**1% Ta$_2$O$_5$**

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

**1% In$_2$O$_3$**

Sintered – TiO$_2$, Rutile
Annealed – TiO$_2$, Rutile
Reduced – TiO$_2$, Rutile

**XRD-Phases**

1% Co$_2$O XRD

Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
Annealed – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
Reduced – (Ti$_{0.1}$Sn$_{0.9}$)O$_2$

1% Mn$_2$O XRD

Sintered – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
Annealed – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
Reduced – (Ti$_{0.1}$Sn$_{0.9}$)O$_2$

Phase Separation
50/50 TiO₂/SnO₂

**XRD-Phases**
- **Sintered** – \((\text{Ti}_{0.8}\text{Sn}_{0.2})\text{O}_2\), \((\text{Ti}_{0.2}\text{Sn}_{0.8})\text{O}_2\), TiO₂
- **Annealed** – \((\text{Ti}_{0.2}\text{Sn}_{0.8})\text{O}_2\), \((\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_2\) @ 1000 °C

1% CoO

1% MnO

**Microstructure Coarsening**
- **@ 1600 °C**

**Grain Boundary Phases Segregation**
Electrical Conductivity

- **Ta₂O₅** – Increases $\sigma - E_a \approx 0.25$ ev
- **(TiₓSn₁₋ₓ)O₂₋y** – Oxygen Deficiency Increases $\sigma - E_a \approx 0.06$ ev
- **Co-doping-Ta₂O₅/CoO** - Increases $\sigma - E_a \approx 0.5-0.7$ ev
- **In₂O₃, MnO & CoO** – Ineffective in Enhancing $\sigma - E_a \approx 1-4.2$ ev
Seebeck Coefficient

75/25 TiO_2/SnO_2

50/50 & 25/75 TiO_2/SnO_2

- N-type
- Large Seebeck coefficients >-400 μV/K
- Large Seebeck coefficient – Low σ
- (Ti_{0.5}Sn_{0.5})O_{2-y} low Seebeck ~ 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.