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.
Thermoelectric Properties of Self Assemble TiO$_2$/SnO$_2$ Nanocomposites

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Ali Sayir, CWRU, USA
Alp Sehirlioglu, CWRU, USA

Program Support: NASA Radioisotope Power Systems
Objective: High Conversion Efficiency
- Reduces Mass, Volume & Cost

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

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

New Approach

Grain Size
- Thermal Aging
- Composition Limited
- Stable

Traditional

Nano-powder Synthesis

Post Process

Nanopowder

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

Cold Densification
- Cold Spray
- Dynamic Compaction
- Plastic Deformation

Thermodynamics
- Phase Transformation
- Precipitation
- Spinodal Decomposition

New Approach

Inhibits Grain Growth
- Rapid Thermal Process
- Inclusions
- Lower Temperature
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>
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</thead>
<tbody>
<tr>
<td>ITO</td>
<td>$8 \times 10^5$</td>
</tr>
<tr>
<td>$\text{In}_2\text{O}_3$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>$\text{SnO}_2$</td>
<td>$2.5 \times 10^5$</td>
</tr>
<tr>
<td>ZnO</td>
<td>$8.3 \times 10^5$</td>
</tr>
<tr>
<td>$\text{ZnO:Al}$</td>
<td>$7.7 \times 10^4$</td>
</tr>
<tr>
<td>$\text{CdSnO}_2$</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 $ZT \sim 0.6$ @ 1000 °C

---

Fig. 10. TEM image of (Ti$_{0.3}$/Sn$_{0.7}$)$_2$O$_3$ ceramics annealed for 48 h. Shultz & Stubican, JACS, 53, 1970
**Experimental**

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

**Dopants**

- CoO
- MnO₂
- Ta₂O₅
- In₂O₃

**Experimental Details**

- **Powder Mixing**
- **Compaction**
- **Die Press**
- **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

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

50/50 TiO_2/SnO_2

75/25 TiO_2/SnO_2

1625 °C

1550 °C

---

**SnO_2 Sintering-Inhibited**

- Surface Diffusion <1100 °C
- Evaporation >1100 °C

SnO_2 → SnO + ½O_2(g)

---

**Sintering Aids-SnO_2**

- MnO, CoO, CuO, ZnO

CoO → Co_{Ti,Sn}'' + O_{V'O}

---

**Phase Separation**

Ta_2O_5 & In_2O_3

Ineffective Sintering Aids

Ta_2O_5 → 2Ta_{Ti,Sn}^* + 2e^* + ½O_2

In_2O_3 → 2In_{Ti,Sn}^* + 2V_O^*
75/25 TiO2/SnO2

Undoped

1% Ta2O5

1% In2O3

XRD-Phases
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

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

Phase Separation

1% Ta2O5

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

XRD-Phases
Sintered – (Ti₀.₈Sn₀.₂)O₂
(Ti₀.₂Sn₀.₈)O₂
TiO₂
Annealed – (Ti₀.₁Sn₀.₉)O₂
1000 °C (Ti₀.₀Sn₀.₁)O₂

XRD-Phases
Sintered – (Ti₀.₈Sn₀.₂)O₂
(Ti₀.₁Sn₀.₉)O₂
Annealed – (Ti₀.₂Sn₀.₈)O₂
1000 °C (Ti₀.₀Sn₀.₁)O₂

1% CoO
1% MnO

Grain Boundary Phases
Segregation

Microstructure
Coarsening
@ 1600 °C
Electrical Conductivity

- Ta$_2$O$_5$ – Increases $\sigma$ – $E_a$$\sim$0.25 ev
- (Ti$_x$Sn$_{1-x}$)O$_{2-y}$ – Oxygen Deficiency Increases $\sigma$ – $E_a$$\sim$0.06 ev
- Co-doping-Ta$_2$O$_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

50/50 & 25/75 TiO₂/SnO₂

- N-type
- Large Seebeck coefficients > -400 μV/K
- Large Seebeck coefficient – Low σ
- \((\text{Ti}_{0.5}\text{Sn}_{0.5})\text{O}_{2-y}\) low Seebeck ~ 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 $\sim$ 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-25 TiO$_2$
- 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.