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
Objective: High Conversion Efficiency
● Reduces Mass, Volume & Cost

Space Power Generation

- Specific Power (W/kg)
  - ZT_{ave} \approx 2.0
  - ZT_{ave} \approx 1.1 (2x Improvement)
  - ZT_{ave} \approx 1.6 (3x Improvement)
  - ZT_{ave} \approx 0.75 (Nano Si-Ge)
  - ZT_{ave} \approx 0.88 (Zintl/Nano Si-Ge)
  - ZT_{ave} \approx 0.55 (RTG Si-Ge)

Conversion Efficiency (%)

Waste Heat to Power

- Waste Heat is one of our most under utilized energy resources
- U.S.-energy consumption \approx 29 \text{ tera-kWh} (10^{12})
  - Barrels of Oil – 170 \text{ giga-barrels} (10^9)
- World-energy consumption \approx 120 \text{ 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.

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

Traditional

Nano-powder Synthesis

Nano-Powder

Post Process

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

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

TiO$_2$ – SnO$_2$

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)</th>
<th>@ RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>$8 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>$1 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>$2.5 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>$8.3 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>$7.7 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>CdSnO$_2$</td>
<td>$7.7 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>CdO:In</td>
<td>$1.7 \times 10^6$</td>
<td></td>
</tr>
</tbody>
</table>

ZnO:Al
ZT~0.6 @ 1000 °C

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

**Experimental**

**Powder Mixing**

**Compaction**

**Reactive Sintering**
- 1250-1550 °C

**Anneal**
- 72 Hrs

**Seebeck/Resistivity**
- ZEM-3
- 6-22 mm
- 4-8 mm

ΔT 0-50 °C/Furnace RT-1000 °C

**Thermal Conductivity**
- Laser Flash Method - Thermal Diffusivity
- Standard
- Specific Heat - C$_p$ - Laser Flash
- Thermal Conductivity (K = αρC$_p$)
Sintering

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

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

CoO → CoTi,Sn + VO²⁺

50/50 TiO₂/SnO₂
1625 °C

75/25 TiO₂/SnO₂
1550 °C

Ta₂O₅ & In₂O₃
Ineffective Sintering Aids

Ta₂O₅ → 2Taₐ₁,Sn + 2e⁻ + ½O₂

In₂O₃ → 2Inₐ₁,Sn + 2VO⁺
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$_2$

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

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

**Annealed**
- TiO$_2$, Rutile
- SnO$_2$, In$_2$O$_3$
- SnO$_2$, In$_2$O$_3$

**XRD-Phases**
- **Sintered** – (Ti$_{0.8}$Sn$_{0.2}$)O$_2$
- **Annealed** – (Ti$_{0.9}$Sn$_{0.1}$)O$_2$
  - 1000 ºC
- (Ti$_{0.1}$Sn$_{0.9}$)O$_2$

**Phase Separation**

**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 ºC
- (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 ºC
- (Ti$_{0.1}$Sn$_{0.9}$)O$_2$
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 $^\circ$C  (Ti$_{0.9}$Sn$_{0.1}$)O$_2$

**XRD-Phases**

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

Annealed – (Ti$_{0.2}$Sn$_{0.8}$)O$_2$
1000 $^\circ$C  (Ti$_{0.9}$Sn$_{0.1}$)O$_2$

**Microstructure Coarsening @ 1600 $^\circ$C**

**Grain Boundary Phases Segregation**
Electrical Conductivity

75/25 TiO\textsubscript{2}/SnO\textsubscript{2}

- 1% Ta\textsubscript{2}O\textsubscript{5}
- TiO\textsubscript{2}
- 1% In\textsubscript{2}O\textsubscript{3}
- Undoped
- 1% MnO
- 1% CoO

50/50 & 25/75 TiO\textsubscript{2}/SnO\textsubscript{2}

- (Ti\textsubscript{0.75}Sn\textsubscript{0.25})O\textsubscript{2-x}

\begin{itemize}
  \item Ta\textsubscript{2}O\textsubscript{5} – Increases \( \sigma \) – \( E_a \sim 0.25 \) ev
  \item (Ti\textsubscript{x}Sn\textsubscript{1-x})O\textsubscript{2-y} – Oxygen Deficiency Increases \( \sigma \) – \( E_a \sim 0.06 \) ev
  \item Co-doping-Ta\textsubscript{2}O\textsubscript{5}/CoO - Increases \( \sigma \) – \( E_a \sim 0.5-0.7 \) ev
  \item In\textsubscript{2}O\textsubscript{3}, MnO & CoO – Ineffective in Enhancing \( \sigma \) – \( E_a \sim 1-4.2 \) ev
\end{itemize}
• 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

- 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.