A new class of high ZT doped bulk nanothermoelectrics through bottom-up synthesis

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Solid-state electrical ⇌ thermal conversion

Heat management/refrigeration

Energy harvesting
Thermoelectrics, a tug-of-war of properties!

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

Thermal conductivity

\[ = \kappa_L + \kappa_c \]

- Nano \( \Rightarrow \) \( \kappa_L \downarrow \)
- But \( a^2 \sigma ? \)
- For p- \text{and} n-type ?
High figure of merit nanostructured thermoelectrics

Best materials – Group V + VI, e.g., Bi$_2$Te$_3$

- Quantum confinement
  - Increase $\sigma$ and $\alpha$
- Interface phonon scattering
  - $\kappa$ decrease
Surfactant-directed nanostructure sculpting and assembly

Surfactant-induced branching through twinning

• Core-shell structures
• Nanoscale features controlled by beaker processing
  – Twining about (221) mirror plane

Sulfurized antimony selenide: nanowire $\rightarrow$ nanotube conversion

- Large $\alpha \sim 1600 \, \mu V/K$
- Low $\sigma \sim 10^{-2} - 10^{-5} \, \Omega^{-1} m^{-1}$
- $\uparrow$ Microwave dose: nanowire $\rightarrow$ nanotube
- TGA $\rightarrow$ sulfurization

Colossal electrical conductivity enhancement in Sb$_2$Se$_3$

- $10^4$-$10^{10}$ higher than bulk; get $\sigma \sim 10 - 10^5 \, \Omega^{-1}m^{-1}$
- Only nanowires (S gradients) show
  - high $\sigma$ and ambient sensitivity
  - Shallow dopant levels from sulfur-surface states

Te-heterostructuring-induced $\alpha$ tuning

- $\alpha$ greater than bulk
  - Heterointerfaces
  - hot carrier filtering

Single-crystal chalcogenide nanoplates and their assemblies

- Shaping, sizing, doping and nanostructure/electronic structure control
  - High ZT; both n- and p-type
  - Very low $\kappa$ and potential for $\alpha^2\sigma$ enhancement

Pnictogen chalcogenide nanoplate building blocks

ZT increase for n- and p-type nanobulk thermoelectrics

- ZT=1.1 n-Bi$_2$Te$_3$, ZT=0.75 p-Sb$_2$Te$_3$ with no alloying!!
- ZT increases monotonically up to 0.95 p-Sb$_2$Te$_3$ at 400 K
- Blind-samples verification at Marlow and Boston College

Stoichiometry, composition

n-type

p-type

Seebck

Te at.%

62

Higher ZT

Nanobulk alloys/composites

Doping

Heterostructuring
50-75% $\kappa_L$ diminution due to nanograin and nanopores

Isotropic properties of bulk-nano thermoelectrics

- Random texture
- Isotropic properties
- Near-stoichiometric
- 0.01-0.25 at.% S doping

\[ p-\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \]

Electrical conductivity \( \sigma \times 10^5 (\Omega^{-1} \text{m}^{-1}) \)

Axial (A) Radial (R)

\begin{align*}
\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 & \quad \text{Bi}_2\text{Te}_3 & \quad \text{Sb}_2\text{Te}_3 \\
1.5 & \quad 2.0 & \quad 1.5 \\
1.0 & \quad 1.5 & \quad 1.0 \\
0.5 & \quad 1.0 & \quad 0.5 \\
0.0 & \quad 0.5 & \quad 0.0
\end{align*}

Sulfur doping and oxidation resistance

- **Sulfur is in different chemical states**
- **Surfactant capping inhibits oxidation**
  - No oxygen-free handling needed
  - Months/years storage in ambient

Effects of sulfur doping on power factor

- High $\alpha$, majority carrier reversal, high $\sigma$
  - S doping, Fermi shift, DoS alteration near Fermi level
  - Non-linear dependence on carrier concentration

Scanning Thermoelectric $\mu$-Probe

- Simultaneous $\kappa$ and $\alpha$ on films and nanobulk
- Non-contact $\kappa$
- Validated using alternative techniques

Nanobulk composite alloys: $\alpha$ tuning, $\kappa_L$ decrease, ZT increase

$\text{Bi}_2\text{Te}_3$ – n-type

$\text{Sb}_2\text{Te}_3$ – p-type

Al-doped ZnO nanocomposites for high ZT @ high T

- Doping + nanostructuring \(\Rightarrow\) ZT=0.45 ….50% increase over bulk at 1000 K

Ultralow thermal conductivity due to nanostructuring

- Nanograins, nanoprecipitates, nanopores
  - 20-fold lower $\kappa$ than bulk

Retention of high $\alpha$ and $\sigma$

- Shallow dopant levels
  - Acoustic phonon scattering at high T—high $\sigma$
  - 40-95% higher $\alpha$ than non-nano $\Rightarrow$ high ZT

Thank you!!