Understanding Thermal Properties in Entropy Stabilized Oxides

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Advanced materials (High Entropy Alloys)

- High Entropy Alloys (HEAs) are 5+ metal components containing high configurational entropy

- HEAs have been demonstrated to possess exceptional properties.

- For high temperature applications, HEAs are especially promising

Lexington @ 2:30 today
Heat transfer mechanisms in Hybrid superlattices
Materials that can withstand temperatures above 2500 °C in oxidizing conditions.

Mixture of MgO, CoO, NiO, CuO, and ZnO that forms a single phase rocksalt crystal at high temperatures.
5- and 6-component (300 nm) thin film samples:

- **5 oxide-component system (5-C)**
  - Equimolar mixture of MgO, CoO, NiO, CuO and ZnO
  - Rocksalt Structure
  - grown at 600° C
  - lattice parameter of 4.29 Å

- **6 oxide-component system (6-C)**
  - Equimolar mixture of MgO, CoO, NiO, CuO, ZnO, and ScO
  - Rocksalt Structure
  - grown at 400° C
  - lattice parameter of 4.18 Å
Pump-probe time delay, $\tau$ (ps)

Thermal model

TDTR ratio, $-X/Y$

TDTR data, 117 nm Al/Si
Pump-probe time delay, $\tau$ (ps)

Thermal model

TDTR ratio, $-X/Y$

TDTR data, 117 nm Al/Si

MgO

ESO film

Transducer

10X Objective

Dichroic Mirror

Lock-in Amplifier

Ti:Sapphire Laser

Beam Splitter

EOM

BiBO

Dichroic Mirror

Delay Stage

Photodetector
Can measure thermal conductivity of thin films and substrates \((k)\) separately from thermal boundary conductance

- Nanometer spatial resolution (~10’s of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact

Typically, can fit for two parameters
4 unknown parameters in model

\[ \begin{bmatrix} C_1 & \kappa_1 & d_1 \\ C_2 & \kappa_2 & d_2 \\ C_3 & \kappa_3 & d_3 \end{bmatrix} \]

parameters in
thermal model
Using modulation frequency to improve sensitivity

- Changing modulation frequency can change parameters to which thermal model is sensitive
- Combined FDTR/TDTR approach allows for fitting multiple parameters

\[ \delta_{\text{thermal}} = \sqrt{\frac{\kappa}{\pi C f}} \]

TDTR Reviews and Analyses
- Rev. Sci. Instr. 75, 5119
- Rev. Sci. Instr. 79, 114902
- J. Heat Trans. 132, 081302
- Ann. Rev. Heat Trans. 16, 159
Measuring Heat Capacity and Thermal Conductivity (300 K)

- Time-domain shows sensitivity to 3 parameters, but unable to decouple heat capacity from thermal conductivity.

- Frequency-domain shows sensitivity to all 4 parameters, and able to decouple heat capacity from thermal conductivity.
Heat capacity of alloys and solid solutions is often taken from literature data for bulk properties of constituent materials.

Rule of mixtures:

\[ C(A_xB_{1-x}) = xC(A) + (1 - x)C(B) \]

\[ C_v(A_xB_{1-x}) = x \frac{\rho_A}{M_A} C_v(A) + (1 - x) \frac{\rho_B}{M_B} C_v(B) \]
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Thermal conductivity ($\kappa$)

$$\kappa = \frac{1}{3} \int C v^2 \tau d\omega$$

$$\tau^{-1} \propto \tau_{\text{mass}}^{-1} + \tau_{\text{strain}}^{-1} + \tau_{\text{volume}}^{-1}$$

More “disorder”
Lower $\kappa$

5-C: $\text{Mg}_x \text{Ni}_x \text{Co}_x \text{Cu}_x \text{Zn}_x \text{O}$
6-C: 5-C+Sc
Scattering mechanisms affecting alloys

Mass impurity scattering in $\text{Si}_x\text{Ge}_{1-x}$ films

$\tau^{-1} \propto \tau_{\text{mass impurity}}^{-1} \propto \Delta M$

Rigorously vetted over time

Can mass impurity explain the decrease from the 5C to the 6C system?

R. Cheaito et al., PRL, 109 (2012)
Thermal conductivity ($\kappa$)

- Thermal conductivity ($\kappa$) vs. Temperature ($T$) graph for different models.
- Temperature $T$ ranges from 70 to 350 K.
- $\kappa$ ranges from 0.5 to 300 W m$^{-1}$ K$^{-1}$.
- Lines represent different models:
  - 6-component model
  - MgO bulk model
  - MgO 300 nm model
  - MgO 300 nm 40% Zn model
  - 5/6-component model

Ingredients:
- MgO
- ZnO
- CuO
- NiO
- CoO

Graphical data and relationships for the 5-component and 6-component ESO models with MgO minimum limit.
Thermal conductivity ($\kappa$) model

- MgO Dispersion


\[
\kappa = \frac{1}{3} C \nu \lambda = \frac{1}{3} C \nu^2 \tau = \frac{1}{3} \sum_j \int_0^{\omega_{max,j}} \hbar \omega D_j(\omega) \frac{\partial f}{\partial T} v^2_j \tau_j d\omega
\]

\[
\tau(k)^{-1} = A \omega^4_j(k) + BT \omega^2_j(k) \exp \left( -\frac{C}{T} \right) + \frac{v_j(k)}{d}
\]

\[
\tau_{m,j}(k)^{-1} = A_j \omega^4(k) = \frac{\Gamma \Omega}{12 \pi v^3_j(k)} \omega^4_j(k)
\]

\[
\Gamma = \sum_i z_i \left( \frac{\Delta M_i}{M} \right)
\]