Application of Ab initio Methods in the Development of Advanced Technical Ceramics

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\[ ZT = \frac{S^2 \sigma T}{\kappa} \]
Vienna Ab-initio Simulation Package

The Vienna Ab-initio Simulation Package, better known as VASP, is a package for performing ab initio quantum mechanical molecular dynamics using either Vanderbilt pseudopotentials, or the projector augmented wave method, and a plane wave basis set.

\[ \psi(x) = E\psi(x) \]

\[
\begin{bmatrix}
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)
\end{bmatrix}
\]

\[
Ce = [\text{Xe}] f^15d^16s^2
\]

\[
O = [\text{He}] 2s^22p^4
\]
Computing Platform

HEWLETT PACKARD HP Z820 WORKSTATION 2 INTEL XENON PROCESSORS ALLOWING 32 CORES FOR CALCULATION WITH 192 GB OF RANDOM ACCESS MEMORY
Dielectric ceramic
A simple case: Cerium Oxide

A change to a simpler symmetry reduces the computational load
Elastic Constants
calculated results for Ceria

\[
c_{ij}[^{\text{GPa}}] = \begin{bmatrix}
455.0683 & 188.74757 & 188.74757 & 0.00000 & 0.00000 & 0.00000 \\
188.74757 & 455.06836 & 188.74757 & 0.00000 & 0.00000 & 0.00000 \\
188.74757 & 188.74757 & 455.06836 & 0.00000 & 0.00000 & 0.00000 \\
0.00000 & 188.74757 & 0.00000 & 81.48183 & 0.00000 & 0.00000 \\
0.00000 & 188.74757 & 0.00000 & 0.00000 & 81.48183 & 0.00000 \\
0.00000 & 188.74757 & 0.00000 & 0.00000 & 0.00000 & 81.48183
\end{bmatrix}
\]

elastic constants \(c_{11}, c_{12}, c_{14}\)
and bulk modulus \((B = 277.52117 \pm 0.348 \text{ (GPa)})\), the mechanical stability criteria
For this case, \(c_{11}\) and \(c_{44} > 0\) \((c_{11} - c_{12})\) and \((c_{11} + 2c_{12})\).
In addition, the bulk modulus must be greater than \(c_{12}\) but less than \(c_{11}\), thus for ceria the mechanical stability requirements are met.
CASTEP Band Structure
Band gap is 2.555 eV

CASTEP Partial Density of States

Energy (eV) vs. Density of States (electrons/eV)
Phonon calculation results
Thermoelectric ceramic
Concept Overview

- Solid state energy harvesting using waste heat available in gas turbine engine offers potential for power generation to meet growing power needs of aircraft
- Thermoelectric material advances offer new opportunities
- Weight-optimized integrated turbine engine structure incorporating energy conversion devices
Complex Skutterudites Thermoelectric (Mackey, Dynys)
Nd0.6Fe2Co2Sb11.85Ge0.15
Characteristics for a desirable thermoelectric material

- Seebeck Coefficient $\sim 100\mu V/K$
- Electrical Resistivity $10^{-2}$ Ohm*cm
- Thermal Conductivity $\sim 10$ W/m*K
- Electronic Band Gap - must be greater than zero
- High Temperature Capability
Experimental 2\textsuperscript{nd} run sample Nd0.6Fe2Co2Sb11.85Ge0.15

VASP-Boltzman Prediction with Chemical potential 1 eV below the Fermi-level
Complex Oxide – based Pyrochlores
mixed cation at B-site $A_2 (B^{3+}, B^{\sim 5+}) O_7$
$Gd_2RuTaO_7$
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Original</th>
<th>change</th>
<th>Final</th>
<th>%</th>
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<td>10.091900</td>
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Volume: 1027.824144 46.795542 1074.619686 4.6

Density: 8.759 Mg/m^3

Elastic constant matrix (GPa):

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<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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Modulus

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<th>Parameter</th>
<th>Voigt</th>
<th>Reuss</th>
<th>Hill</th>
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<tr>
<td>Bulk</td>
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<td>184.23 GPa</td>
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<td>Shear</td>
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<td>89.78</td>
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<td>Young's</td>
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<td>231.59</td>
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<tr>
<td>Longitudinal</td>
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</table>

Velocity of sound

Calculated from Hill moduli:
- transverse waves: 3271 m/s
- longitudinal waves: 6009 m/s
- mean: 3649 m/s

Debye temperature: 465.9 K
the thermal coefficient of linear expansion at 600K = 7.60 x 10^-6
Calculated Electronic Band Structure

Perdew – Ernzerhof – Burke (PBE)

Heyd – Scuseria – Ernzerhof (HSE06)

Cut off energy of 575 eV k-spacing 0.199 Å and 4x4x4 k mesh using DFT PBE the bandgap is 0.07 eV
Electrical Conductivity

Chemical Potential, eV

BoltzTraP. A code for calculating band-structure dependent quantities
Georg K.H. Madsen a,*, David J. Singh b

Computer Physics Communications 175 (2006) 67–71
Temperature dependent Seebeck coefficient

Chemical Potential, eV

- $u = -0.032$
- $u = 0.008$
- $u = 0.089$

Temperature, K

Seebeck Coefficient, μV/K

- 160
- 120
- 80
- 40
- 0

Temperature, K

400 600 800 1000 1200
Molecular Dynamic Computational Results:
Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)

**Buckingham force field:**

LAMMPS
Pressure = 1 atm
Time Step = 1 fs

Thermal Conductivity, W/m*K

Temperature, K
$2\text{Gd}_2\text{O}_3 + \text{Ta}_2\text{O}_5 + 2\text{RuO}_2 \rightarrow 2\text{Gd}_2(\text{Ta, Ru})\text{O}_7 + \frac{1}{2} \text{O}_2$

Solid state reaction, mechanical mixing, sintering in air, hot pressing
Complex Oxide – based Pyrochlores
mixed cation at B-site $A_2 \left( B^{3+}, B^{-5+} \right) O_7$
$Gd_2RuVO_7$
\[2\text{Gd}_2(\text{CO}_3)_3 + \frac{1}{2}\text{V}_2\text{O}_5 + 2\text{RuO}_2 \rightarrow 2\text{Gd}_2 \text{RuVO}_7 + 6\text{CO}_2 + \frac{1}{2}\text{O}_2\]
Experimental Seebeck coefficient and Resistivity data for Gd$_2$ RuVO$_7$
Magnetic material
First-Principle and Experimental Study of a Gadolinium Praseodymium Cobalt Pseudo-binary Intermetallic Compound
<table>
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<td>zero</td>
<td>zero</td>
<td>non-zero</td>
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<td>Spin Density</td>
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<tr>
<td></td>
<td>Density (g/cm³)</td>
<td>Lattice Parameter (Ångstrom)</td>
<td>Magnetization (Amperes*meter² per kg)</td>
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<td>CASTEP</td>
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<td>a=b=8.41, c=12.23</td>
<td>93</td>
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CONCLUSIONS

• Computational methods parameters can be used for predictions and to aid in the development of ceramic materials.

• Some descriptions (band structure) are very sensitive to such things as mesh density.

• Ceramics such oxide pyrochlores have potential as thermoelectric materials.

• Nature is always right!