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

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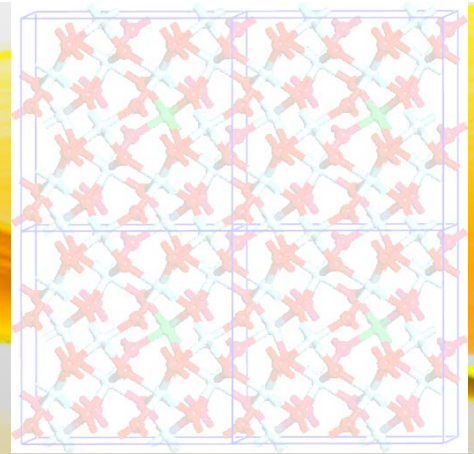
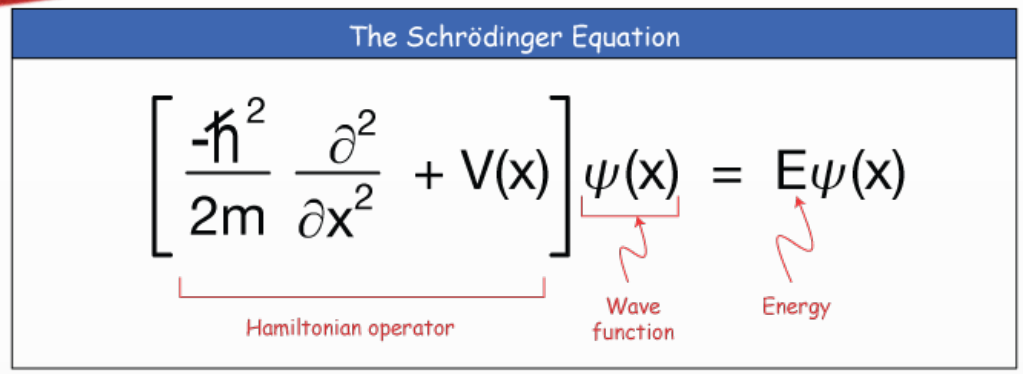
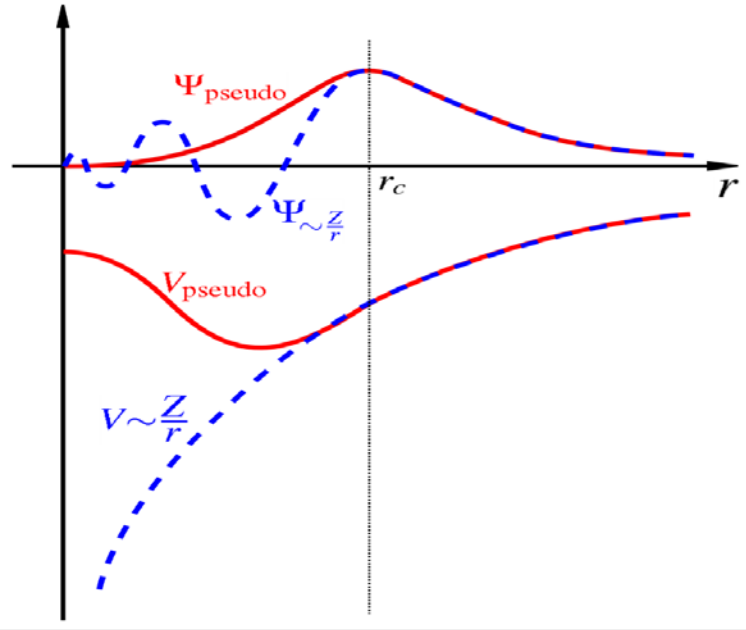


Computational Methods





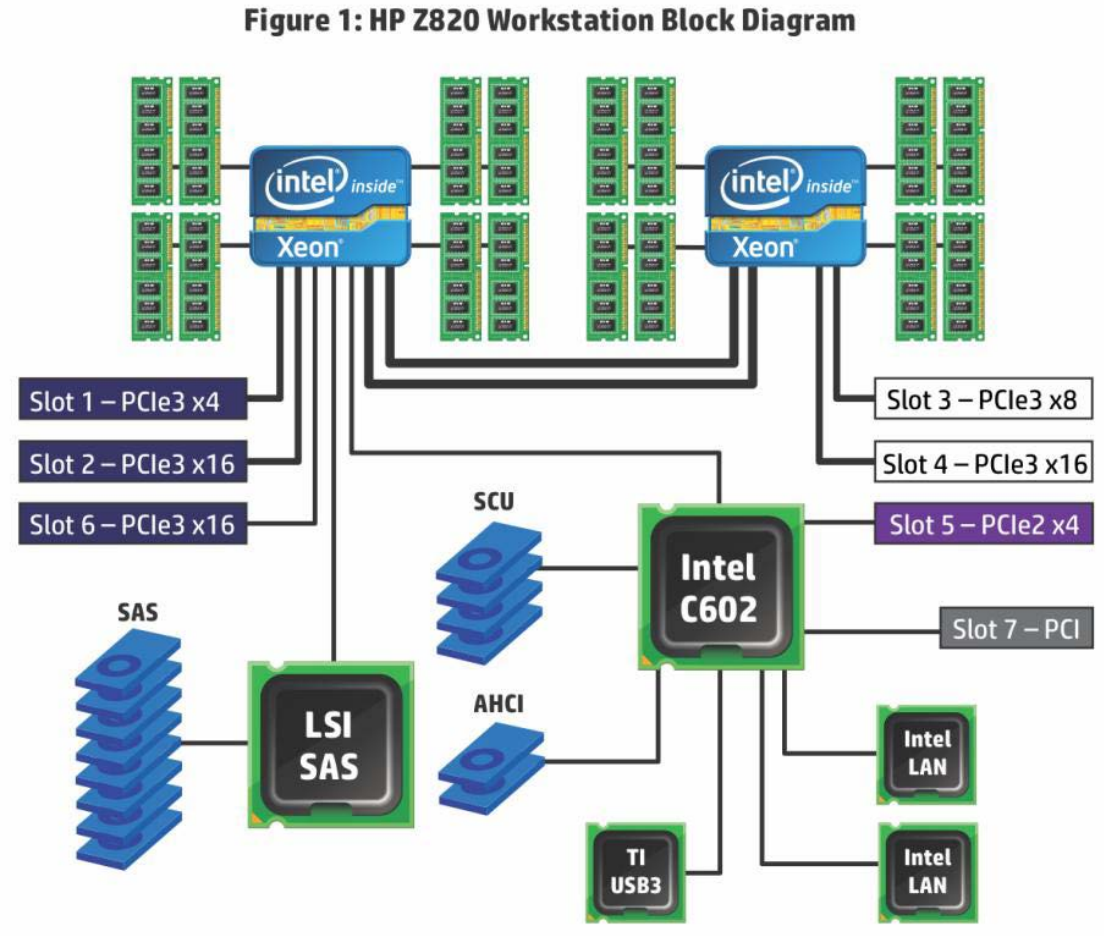
Ce = [Xe] $f^1 5d^1 6s^2$

O = [He] $2s^2 2p^4$

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

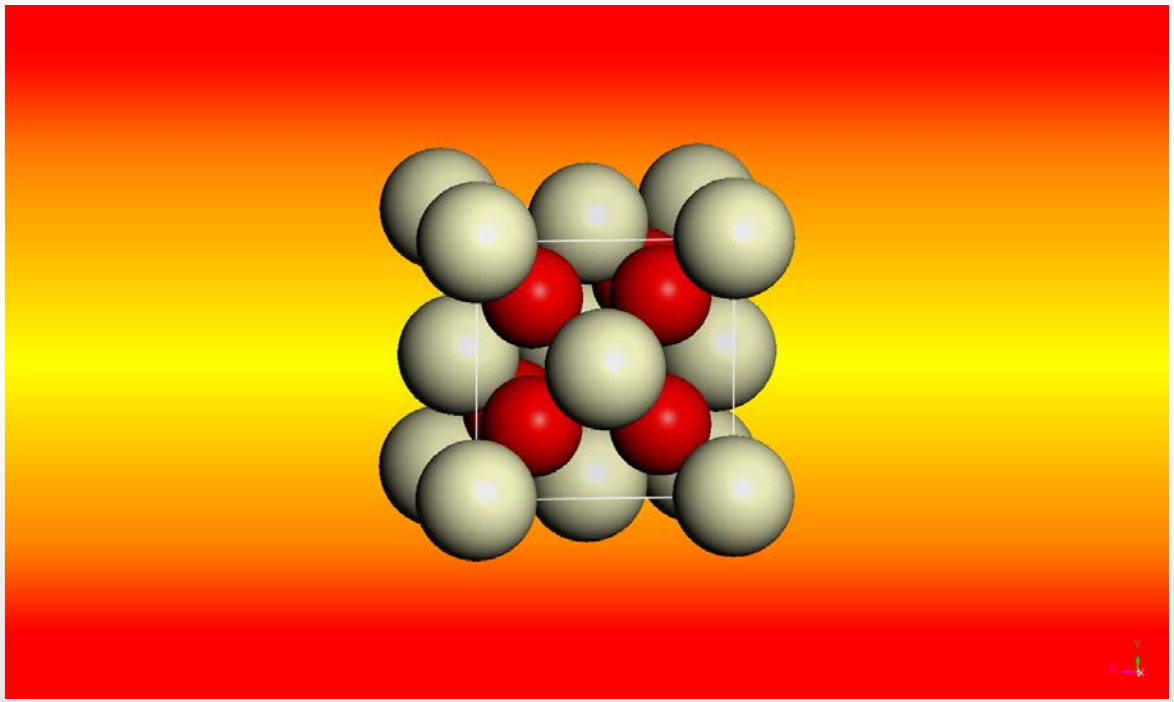
Computing Platform

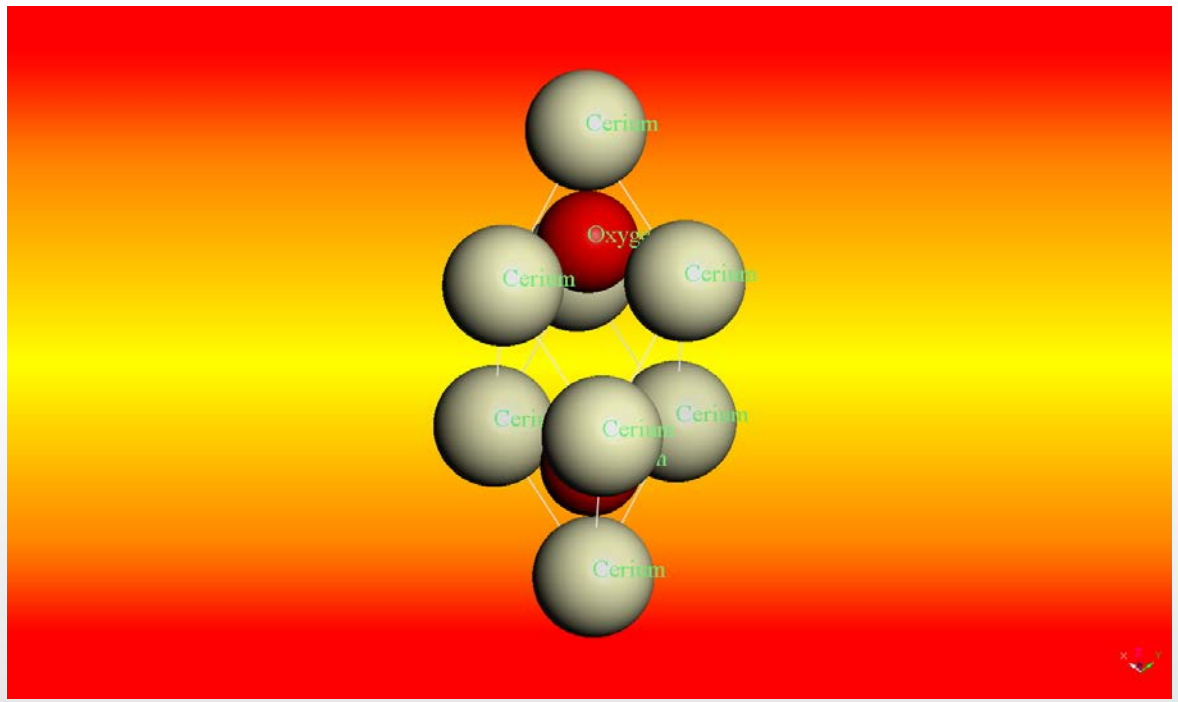


HEWLETT PACKARD HP Z820 WORKSTATION 2 INTEL XENON PROCESSORS ALLOWING 32 CORES FOR CALCULATION WITH 192 GB OF RANDOM ACCESS MEMORY

Dielectric ceramic

A simple case: Cerium Oxide





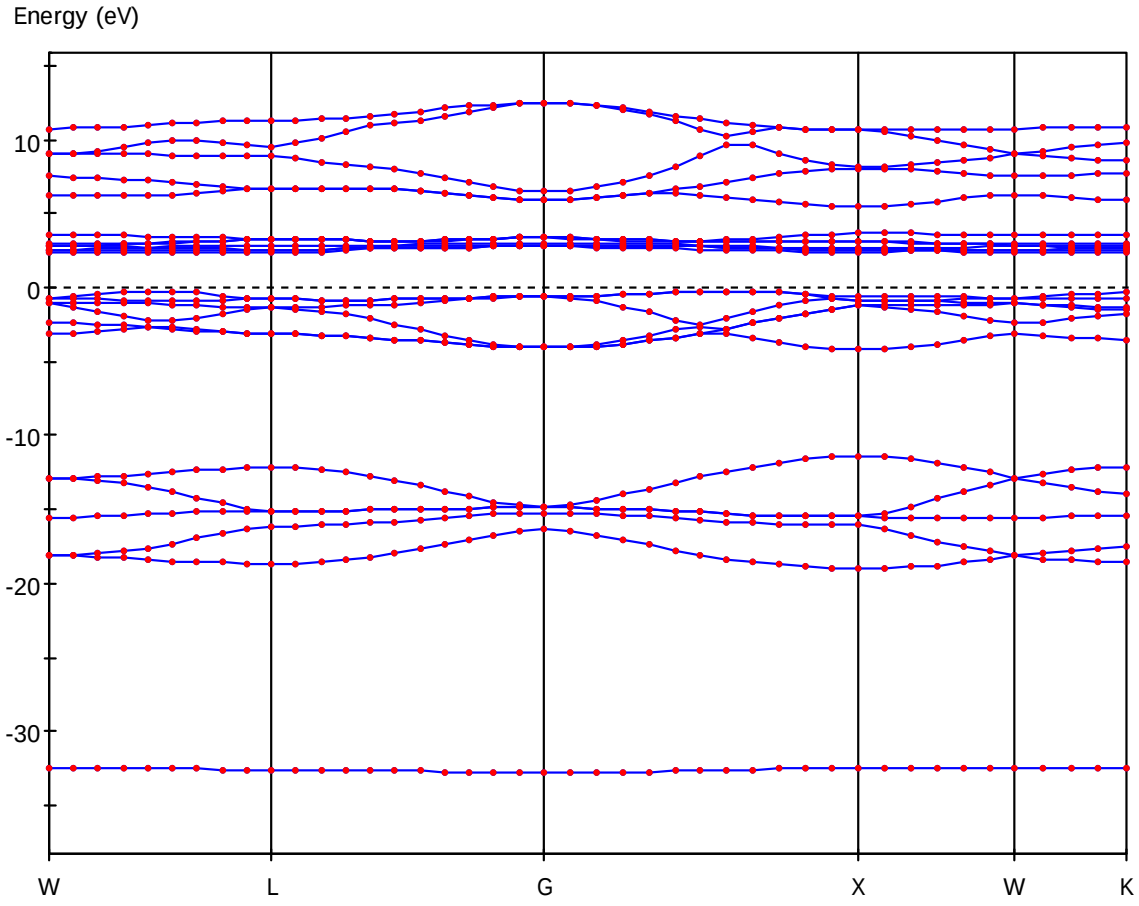
A change to a simpler symmetry reduces the computational load

Elastic Constants
calculated results for Ceria

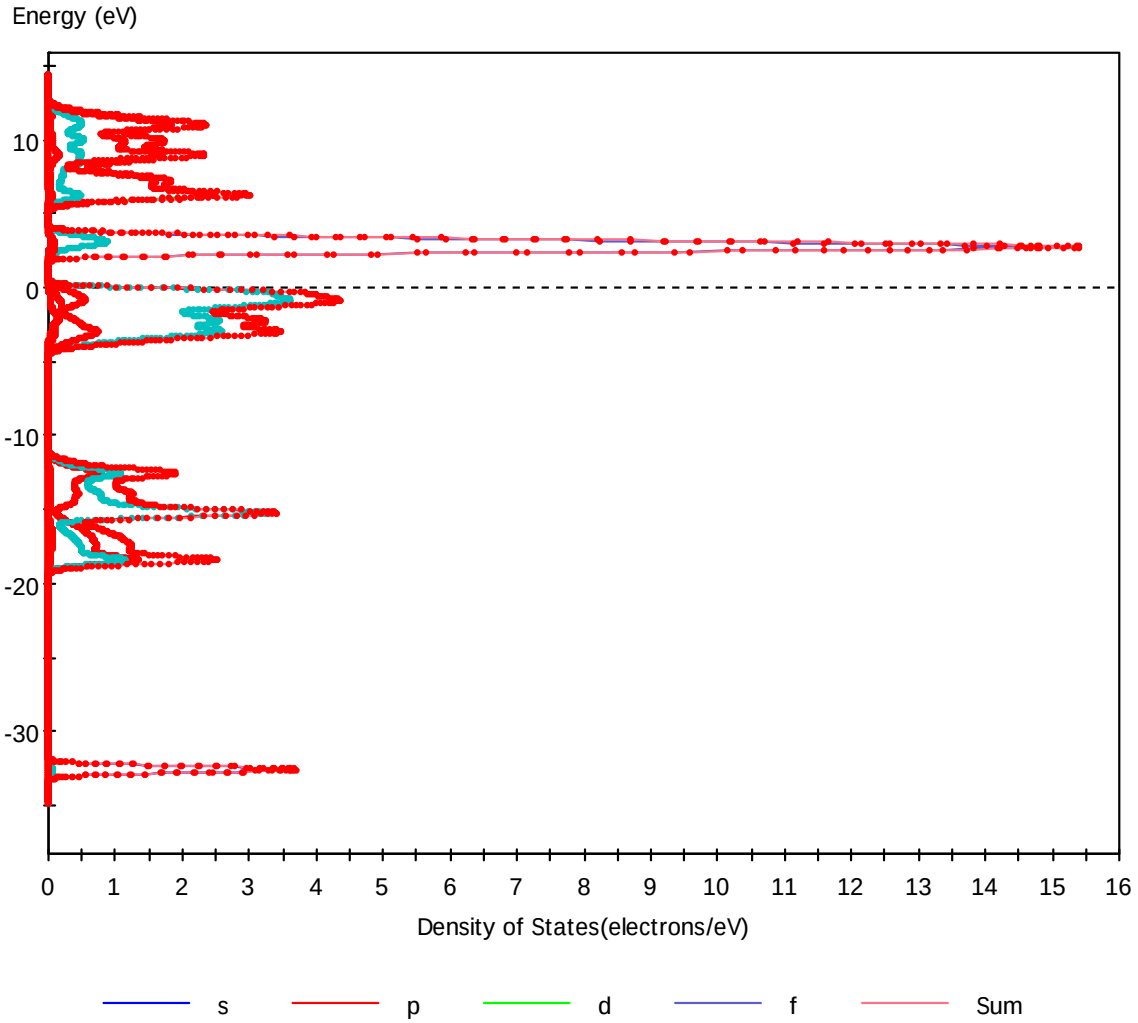
$$cij\left[GPa\right]=\begin{bmatrix} 455.0683 & 188.74757 & 188.74757 & 0.00000 & 0.00000 & 0.00000 \\ 188.74757 & 455.06836 & 188.74757 & 0.00000 & 0.00000 & 0.00000 \\ 188.74757 & 188.74757 & 455.06836 & 0.00000 & 0.00000 & 0.00000 \\ 0.00000 & 188.74757 & 0.00000 & 81.48183 & 0.00000 & 0.00000 \\ 0.00000 & 188.74757 & 0.00000 & 0.00000 & 81.48183 & 0.00000 \\ 0.00000 & 188.74757 & 0.00000 & 0.00000 & 0.00000 & 81.48183 \end{bmatrix}$$

elastic constants c_{11}, c_{12}, c_{14}
and bulk modulus (B = 277.52117 ± 0.348 (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.

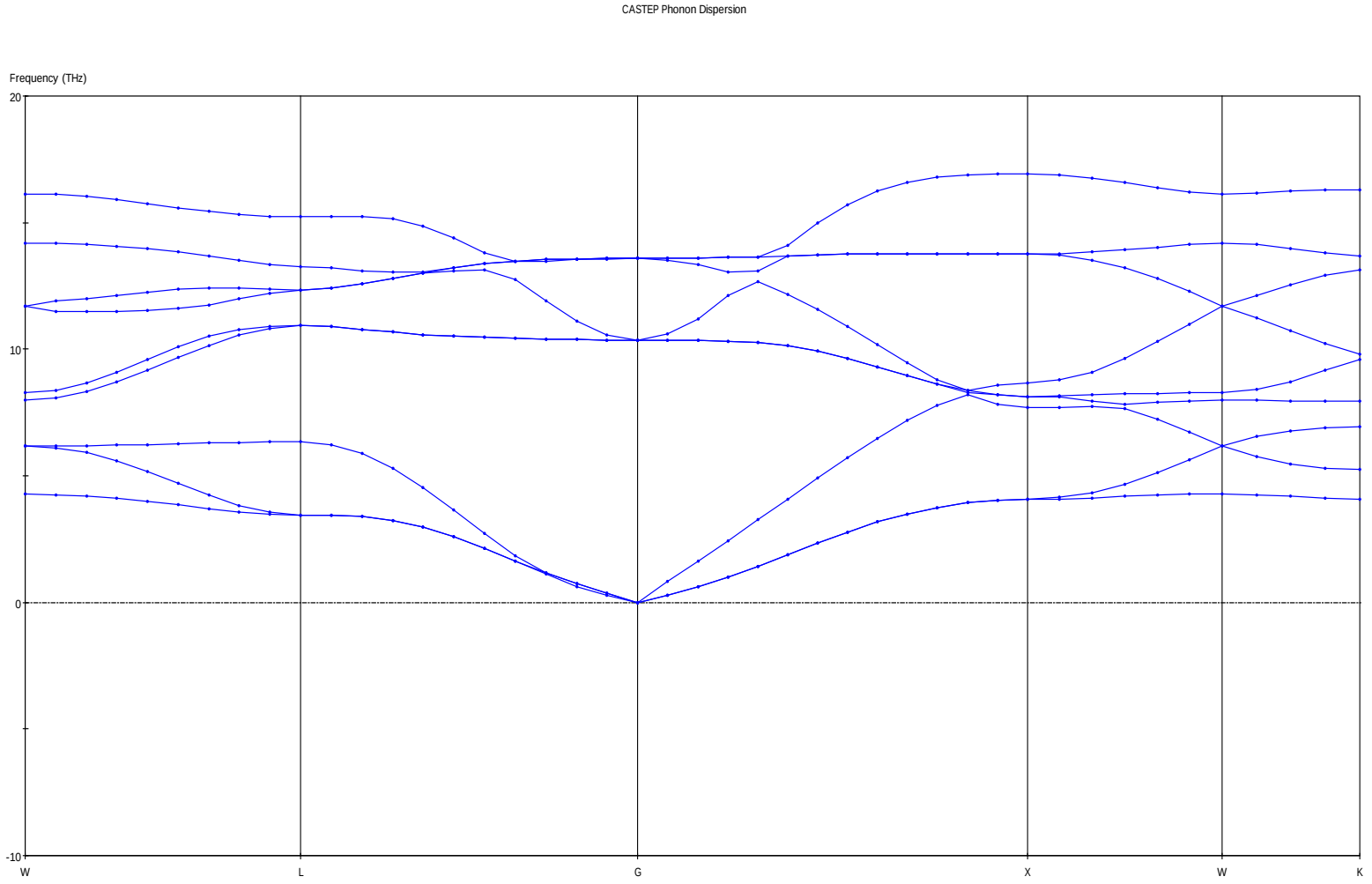
CASTEP Band Structure
Band gap is 2.555 eV



CASTEP Partial Density of States

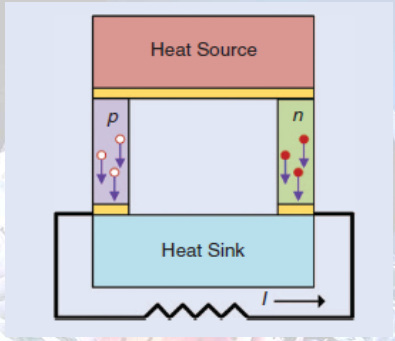


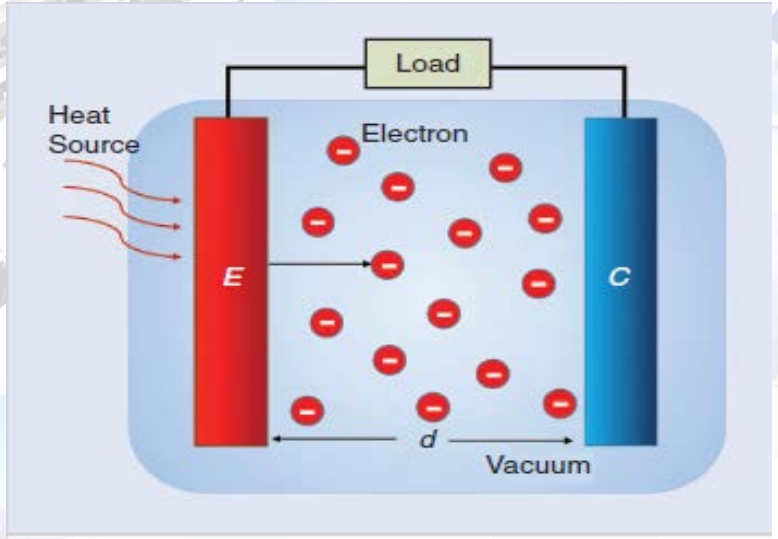
Phonon calculation results



Thermoelectric ceramic

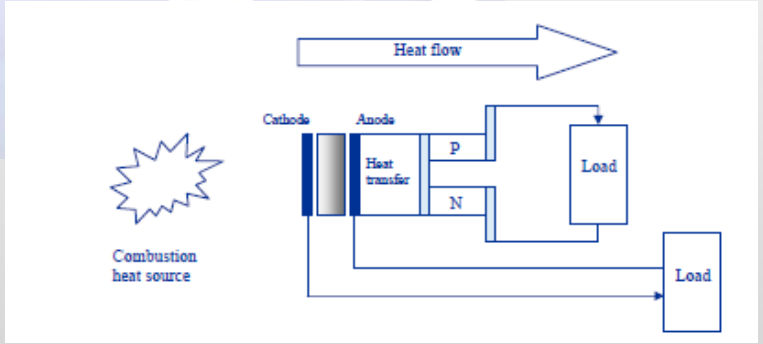
Concept Overview





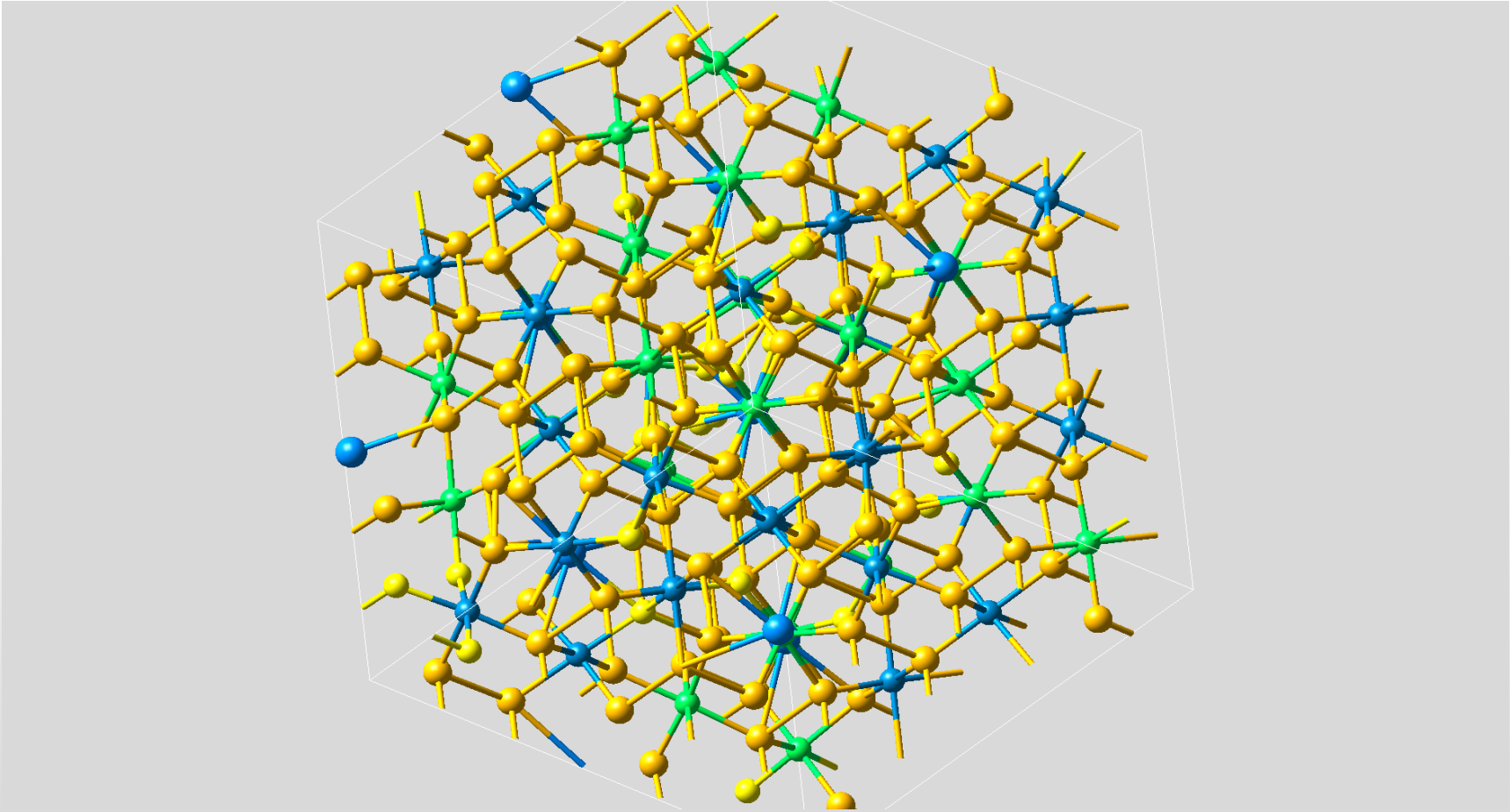
$$J = AT^2 e^{-\left(\frac{E_w}{kT}\right)}$$

- 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



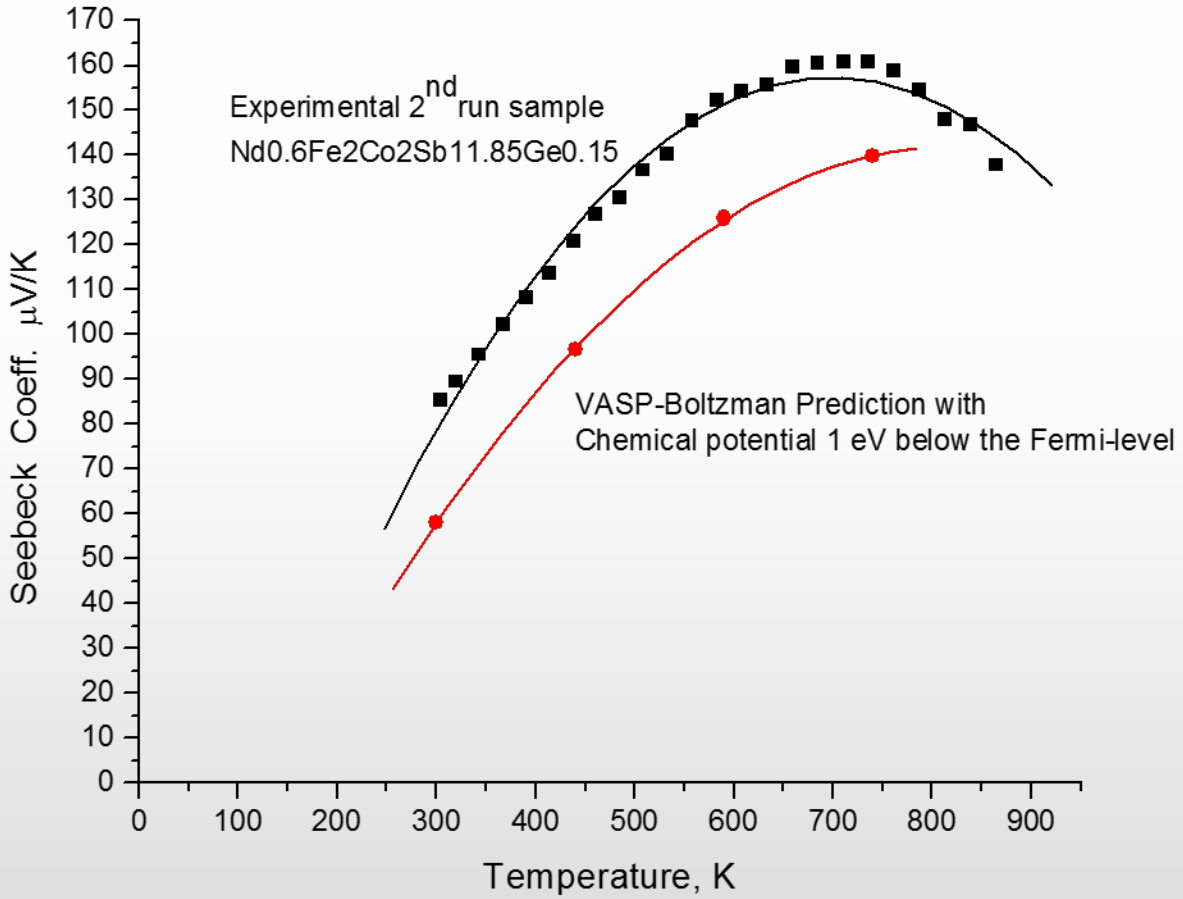
Thermionic
+
Thermoelectric

Complex Skutterudites Thermoelectric (Mackey, Dynys)
$Nd_{0.6}Fe_2Co_2Sb_{11.85}Ge_{0.15}$



Characteristics for a desirable thermoelectric material

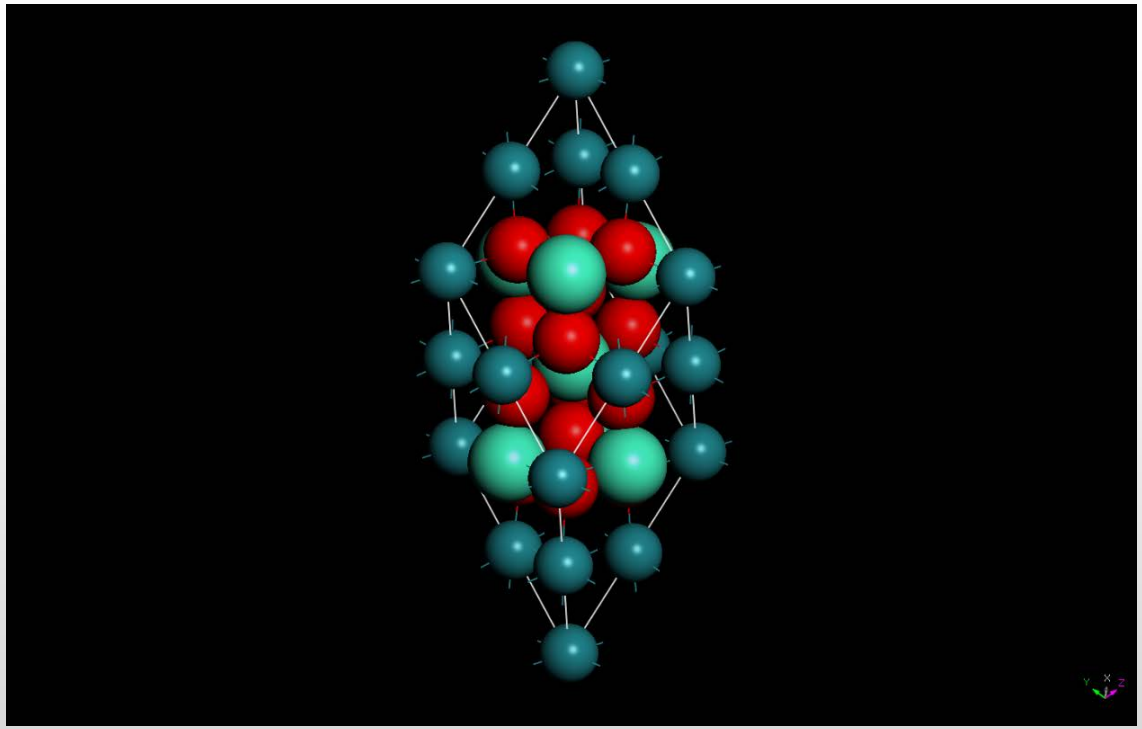
- Seebeck Coefficient ~ 100uV/K
- Electrical Resistivity 10^{-2} Ohm*cm
- Thermal Conductivity ~ 10 W/m*K
- Electronic Band Gap -must be greater than zero
- High Temperature Capability


Experimental 2nd run sample
Nd0.6Fe2Co2Sb11.85Ge0.15
VASP-Boltzman Prediction with
Chemical potential 1 eV below the Fermi-level
Seebeck Coeff. μV/K
Temperature, K
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
0
100
200
300
400
500
600
700
800
900

Complex Oxide – based Pyrochlores

mixed cation at B-site $A_2 (B^{3+}, B^{\sim 5+}) O_7$

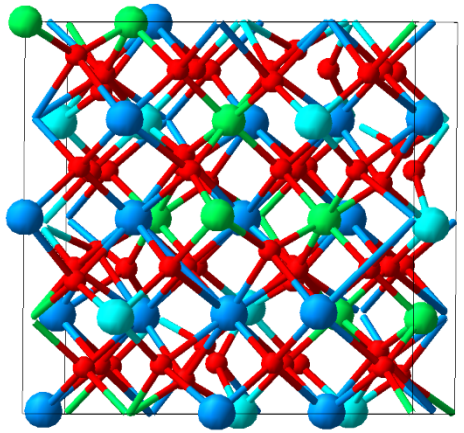
Gd_2RuTaO_7



Calculated Cell Parameters

Parameter	Original	change	Final	%
a	10.091900	0.158505	10.250405	1.6
b	10.091900	0.137867	10.229767	1.4
c	10.091900	0.156757	10.248657	1.6
alpha	90.000000	-0.361354	89.638646	-0.4
beta	90.000000	0.392175	90.392175	0.4
gamma	90.000000	0.047839	90.047839	0.1
Volume	1027.824144	46.795542	1074.619686	4.6

Density: 8.759 Mg/m^3



Elastic constant matrix (GPa):

	1	2	3	4	5	6
1	303.99	122.74	112.40	0.00	0.00	0.00
2	122.74	342.62	128.66	0.00	0.00	0.00
3	112.40	128.66	289.89	0.00	0.00	0.00
4	0.00	0.00	0.00	98.03	0.00	0.00
5	0.00	0.00	0.00	0.00	76.22	0.00
6	0.00	0.00	0.00	0.00	0.00	88.62

Modulus	Voigt	Reuss	Hill
Bulk	184.90	183.56	184.23 GPa
Shear	90.75	89.78	90.27
Young's	233.98	231.59	232.78
Longitudinal			304.59

Velocity of sound

Calculated from Hill moduli:

transverse waves: 3271 m/s

longitudinal waves: 6009 m/s

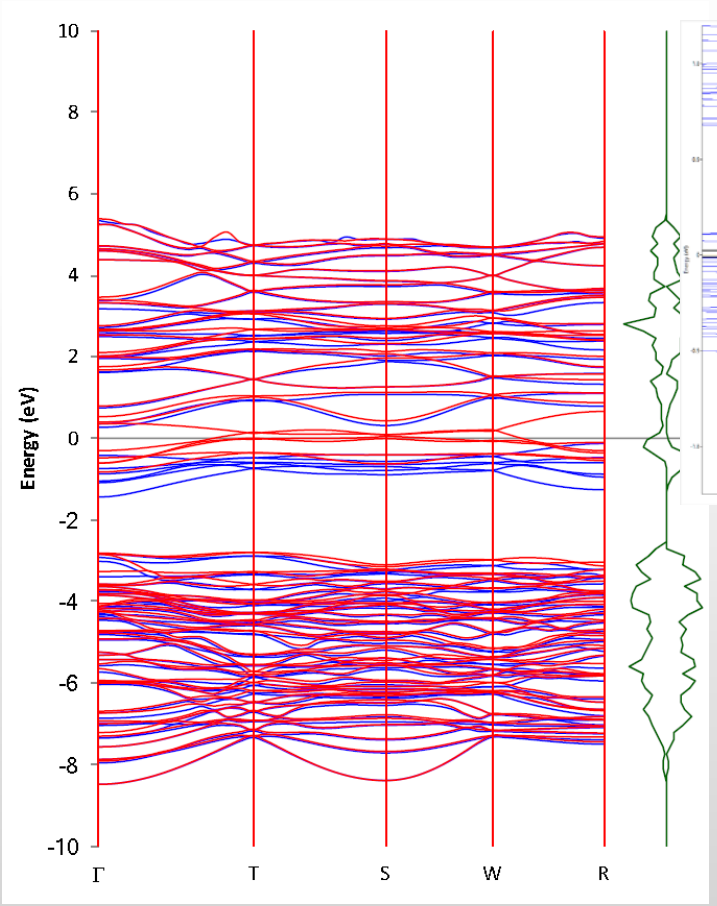
mean: 3649 m/s

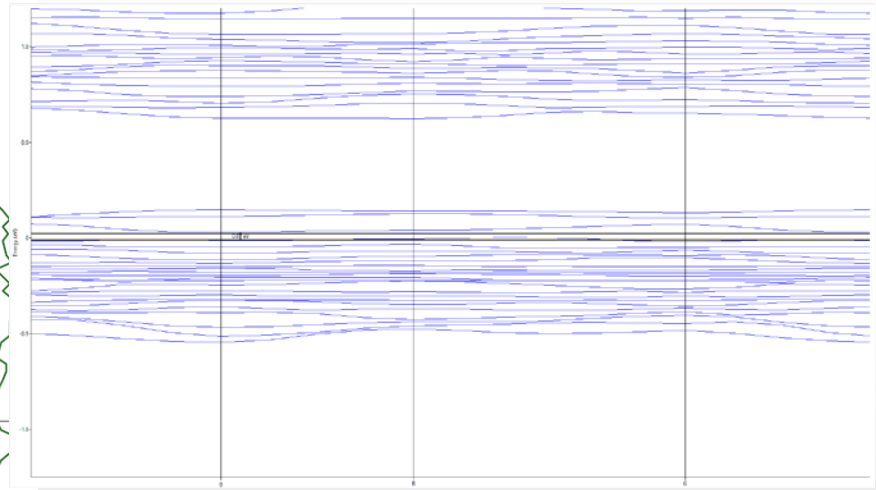
Debye temperature: 465.9 K

the thermal coefficient of linear expansion at 600K = 7.60×10^{-6}

Calculated Electronic Band Structure

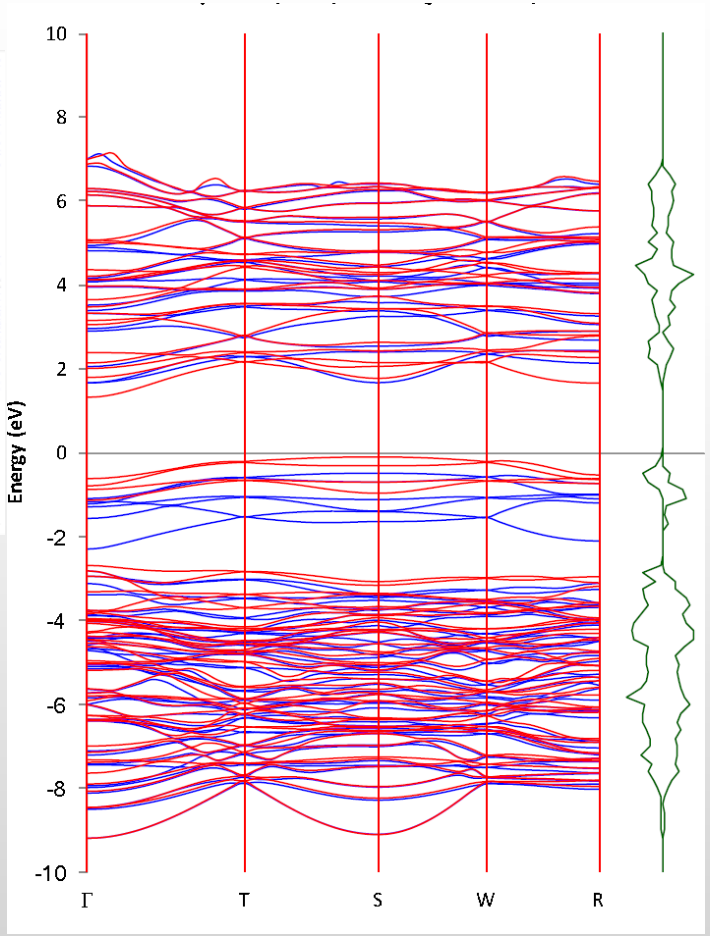
Perdew – Ernzerhof – Burke (PBE)



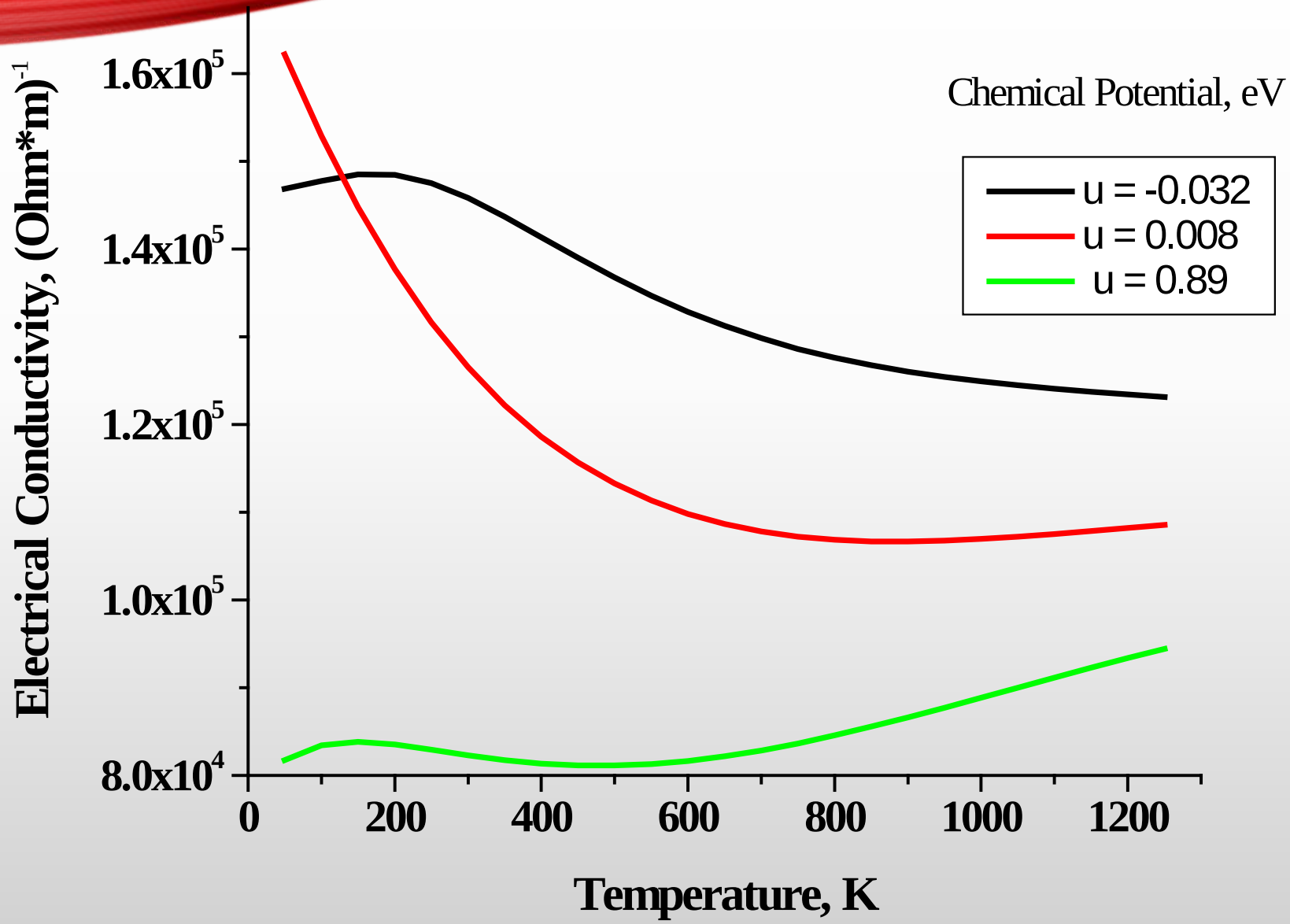


Cut off energy of 575 eV k-spacing 0.199/ A and 4x4x4 k mesh using DFT PBE the bandgap is 0.07 eV

Heyd –Scuseria -Ernzerhof (HSE06)



Electrical Conductivity

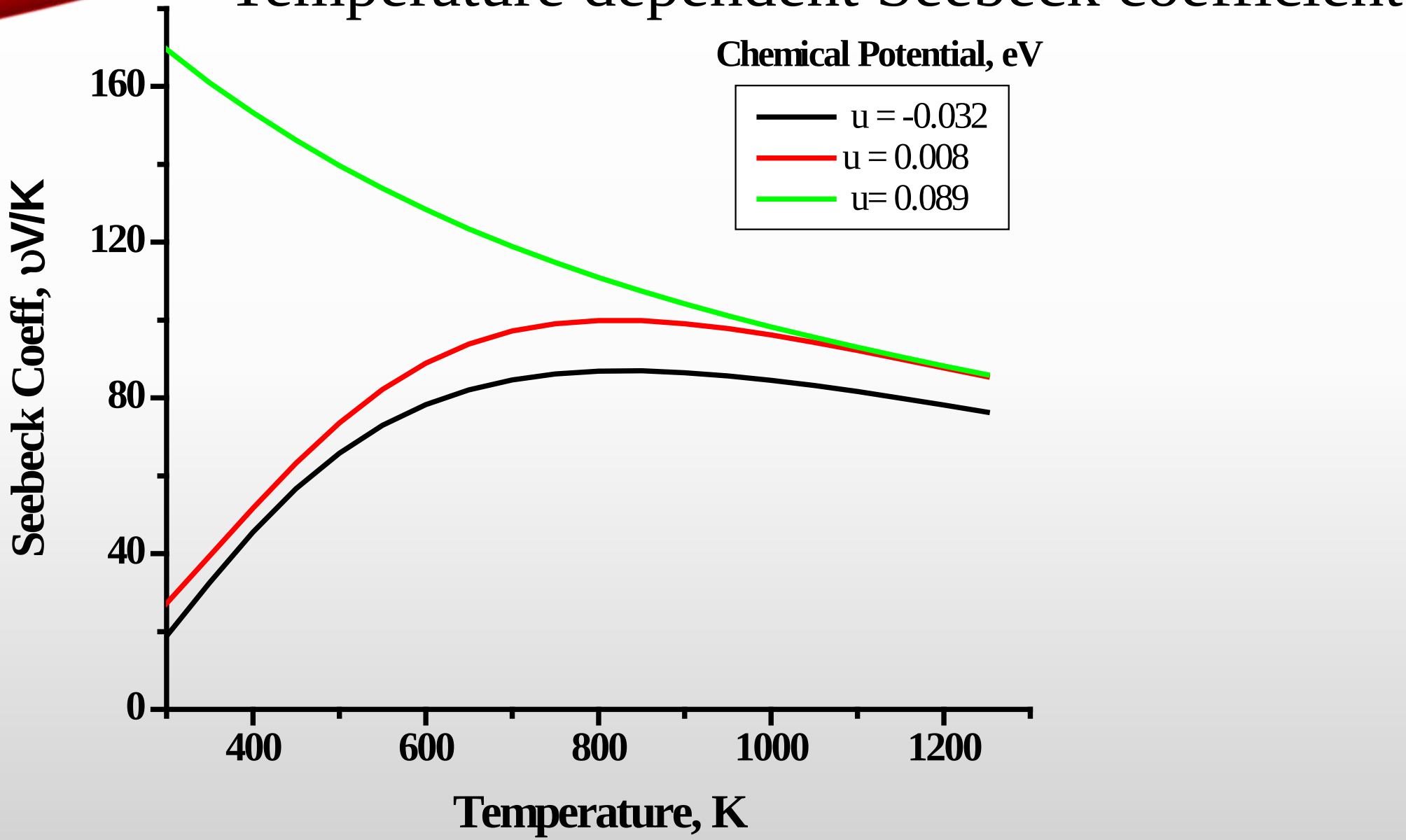


BoltzTraP. A code for calculating band-structure dependent quantities ☆

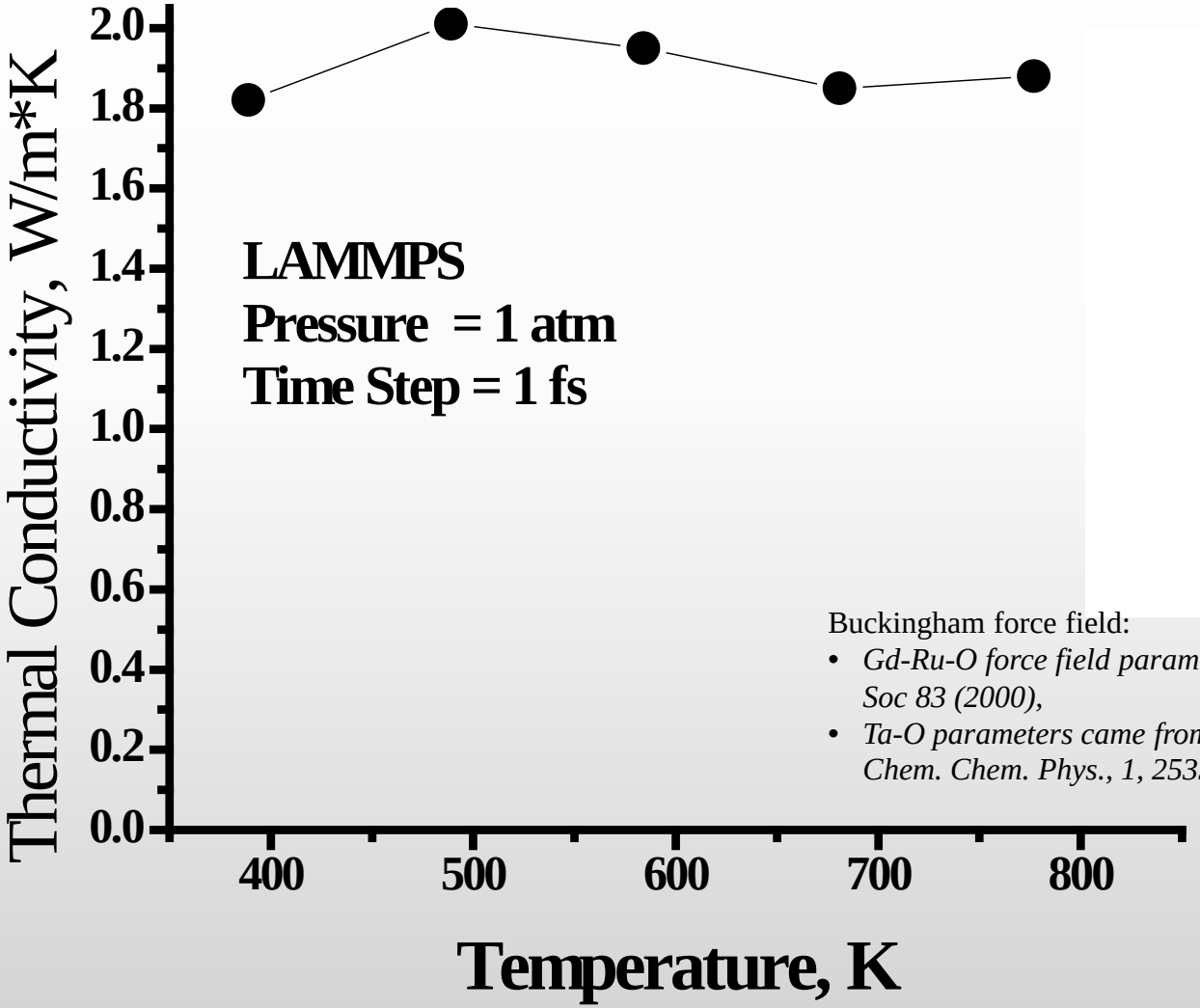
Georg K.H. Madsen [a,*], David J. Singh [b]

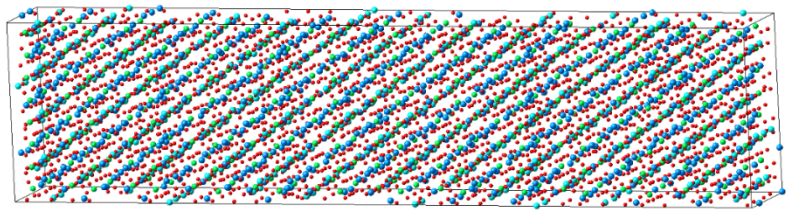
Computer Physics Communications 175 (2006) 67–71

Temperature dependent Seebeck coefficient



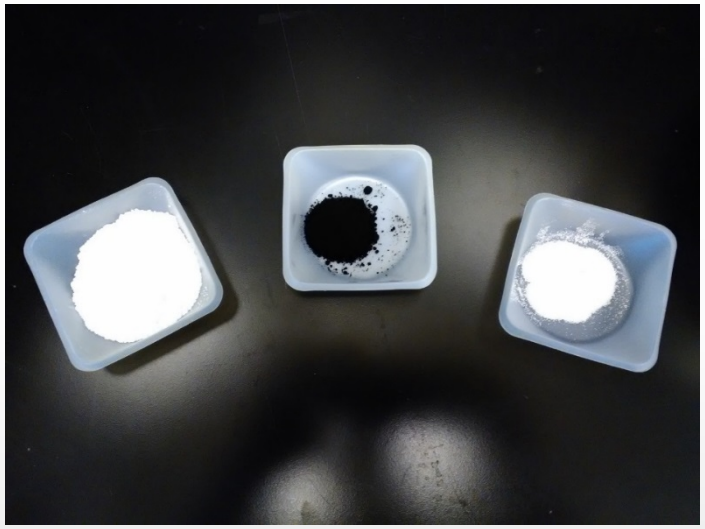
Molecular Dynamic Computational Results:
Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)

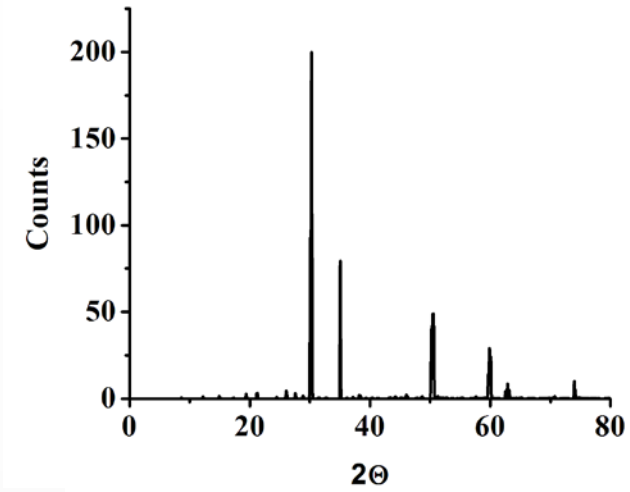


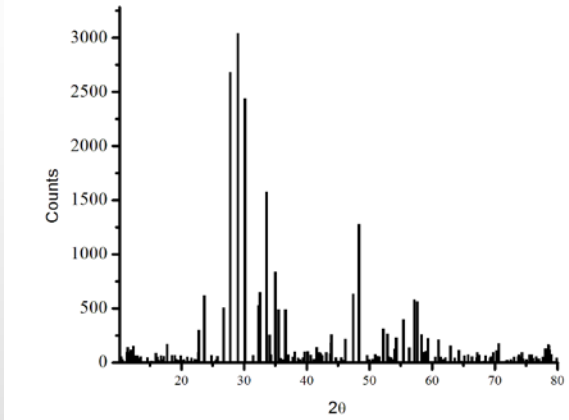


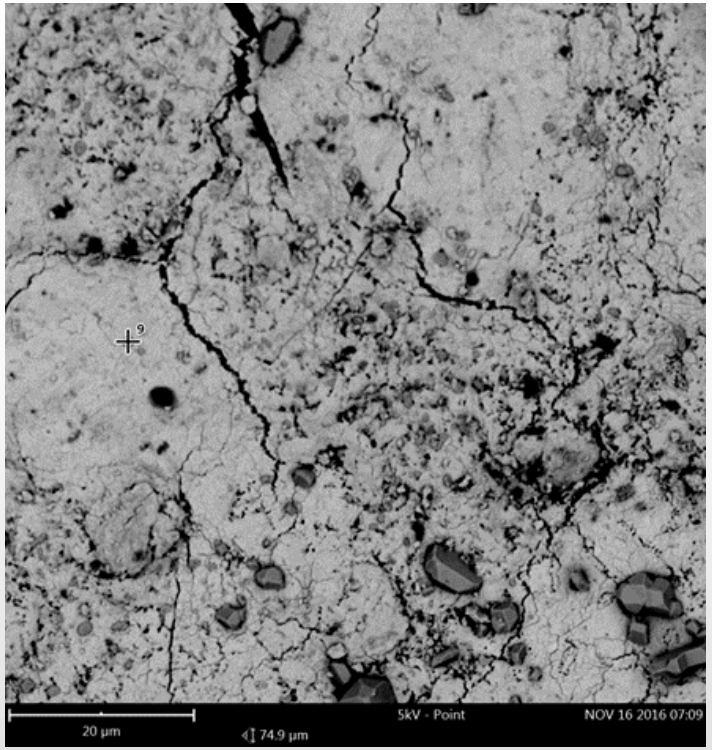
Buckingham force field:

- *Gd-Ru-O force field parameters came from Minervini, RW Grimes, KE Sickafus J Am Ceram Soc 83 (2000),*
- *Ta-O parameters came from S.M.Woodley, P.D.Battle, J.D.Gale and C.R.A.Catlow Phys. Chem. Chem. Phys., 1, 2535-2542 (1999).*









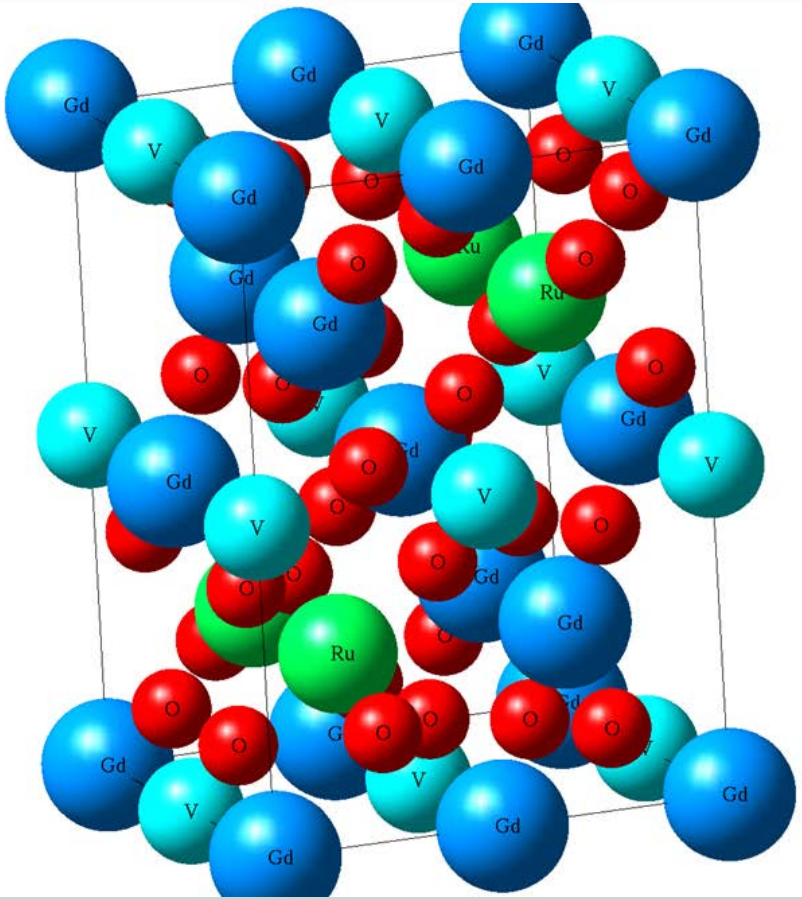
$$2Gd_2O_3 + Ta_2O_5 + 2RuO_2 \longrightarrow 2Gd_2(Ta, Ru)O_7 + ½\ O_2$$

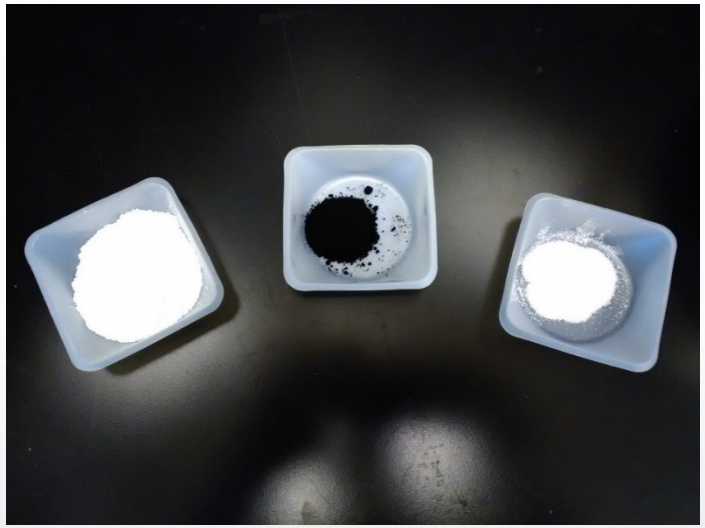
Solid state reaction, mechanical mixing, sintering in air, hot pressing

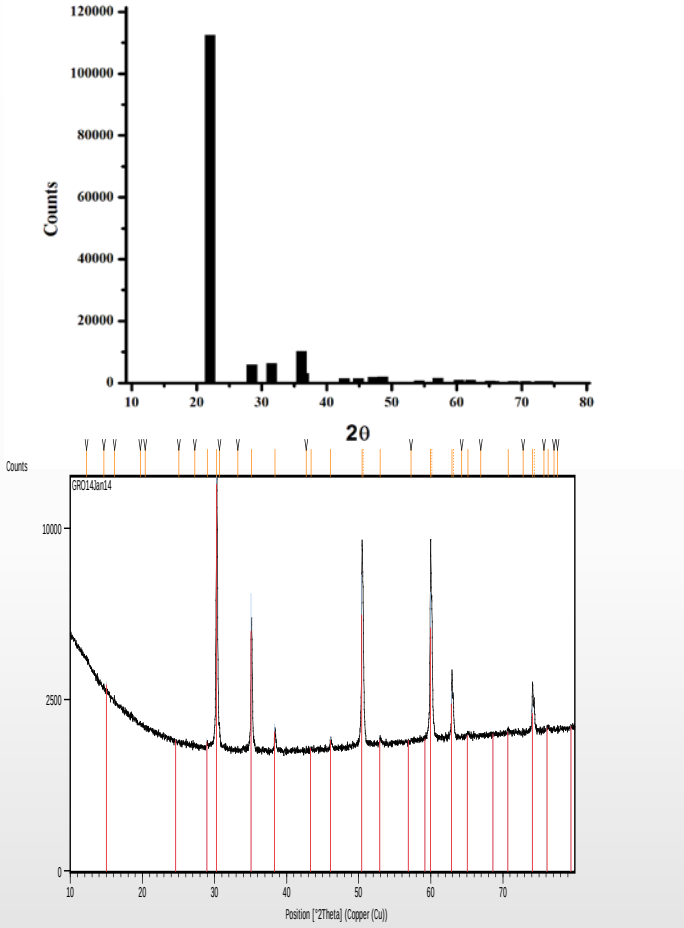
Complex Oxide – based Pyrochlores

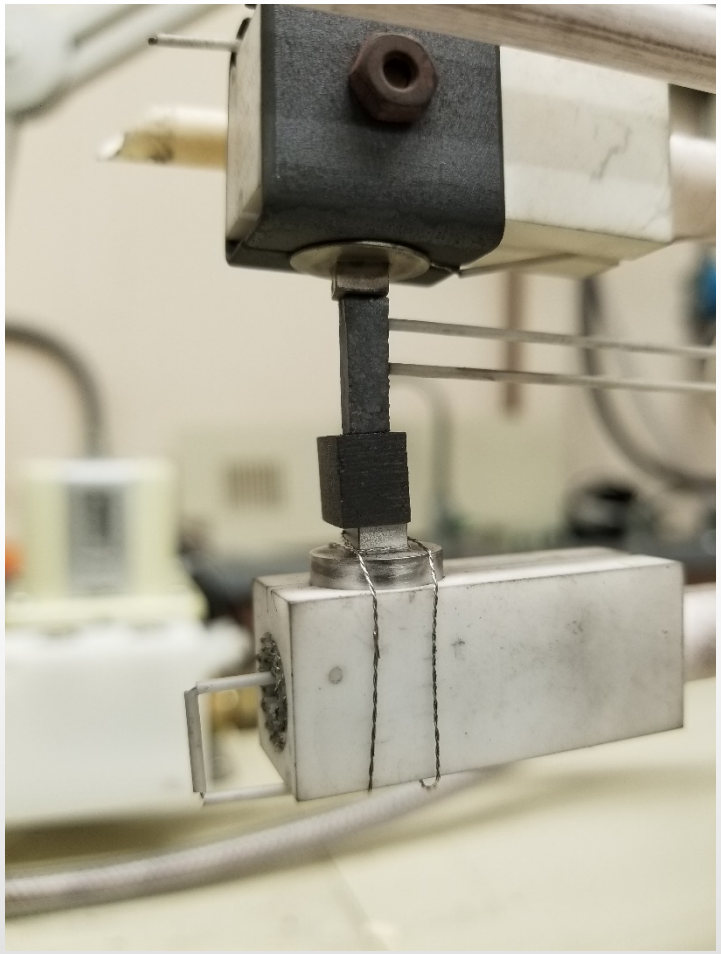
mixed cation at B-site $A_2 (B^{3+}, B^{\sim 5+}) O_7$

Gd_2RuVO_7



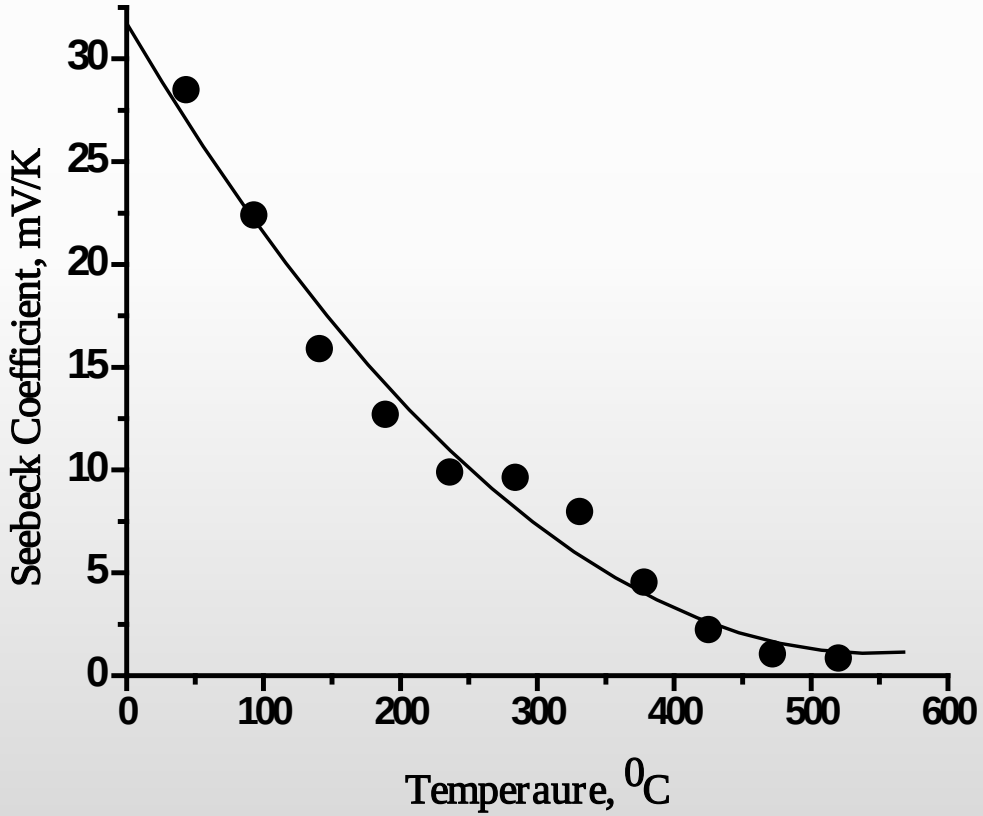


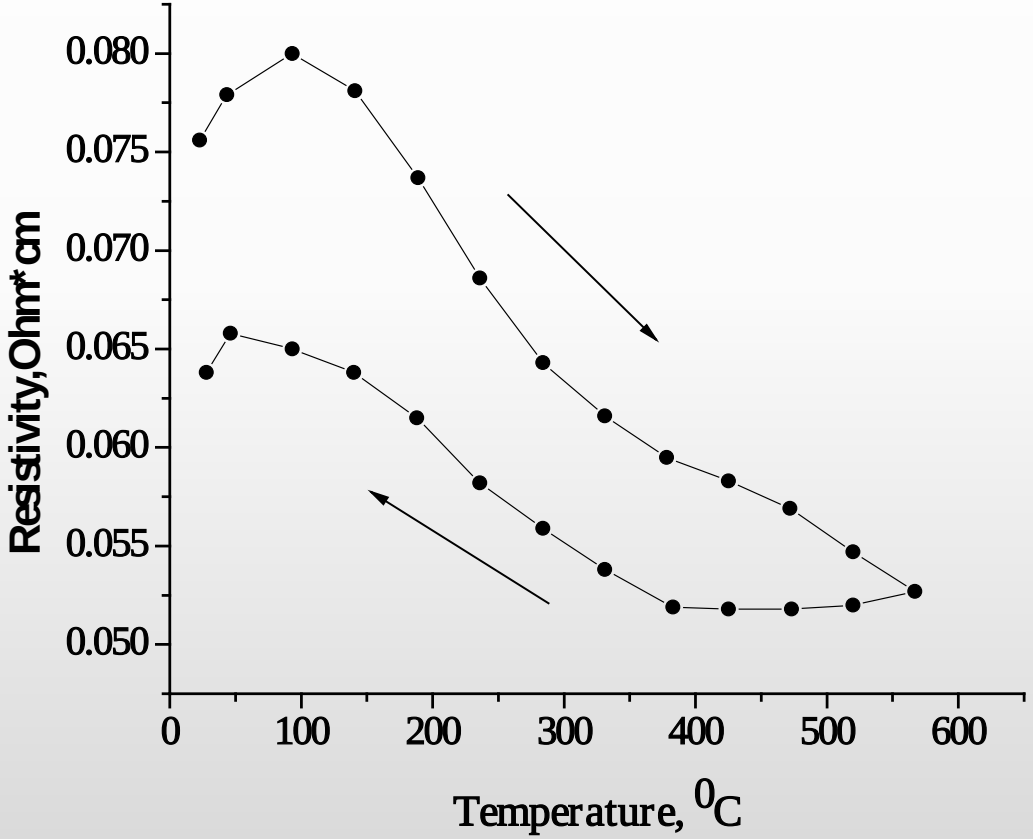




$$2Gd_2(CO_3)_3 + 1/2V_2O_5 + 2RuO_2 \longrightarrow$$
$$2\ Gd_2\ RuVO_7 + 6CO_2 + 1/2O_2$$

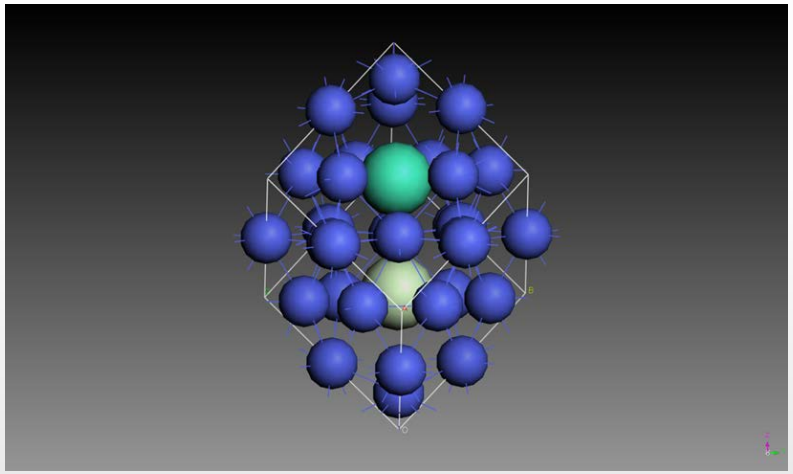
Experimental Seebeck coefficient and Resistivity data for $Gd_2 RuVO_7$

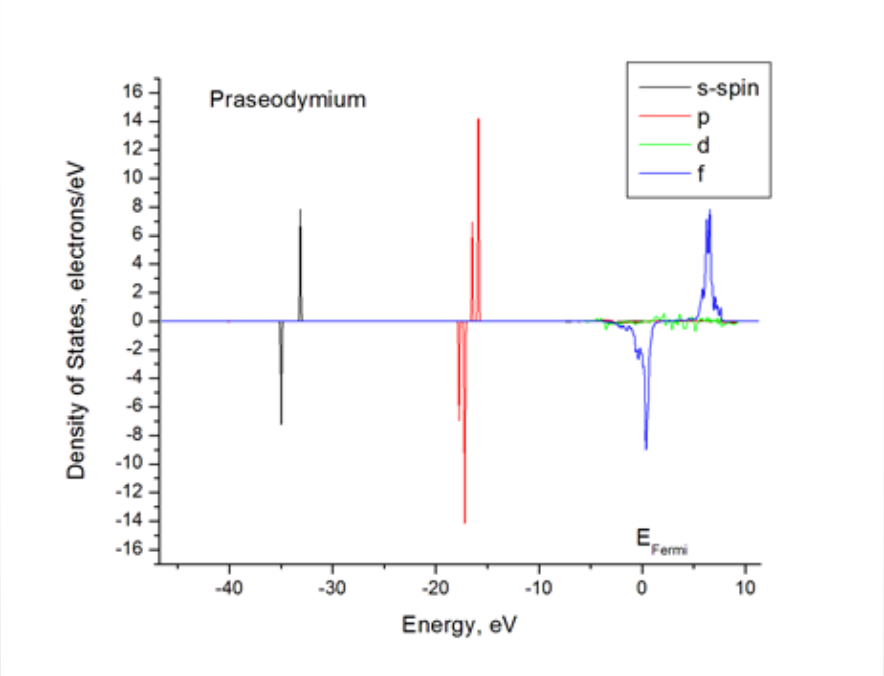


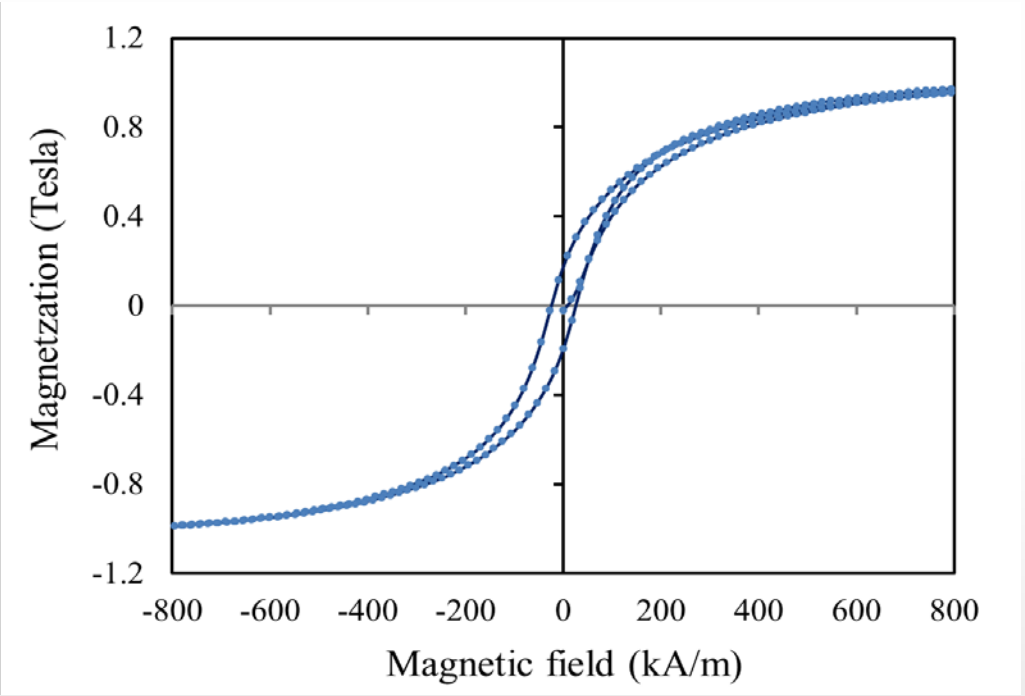


Magnetic material

First-Principle and Experimental Study of a Gadolinium Praseodymium Cobalt Pseudo-binary Intermetallic Compound







Parameter	Ferromagnetic	Paramagnetic	Antiferromagnetic	Ferrimagnetic
2*Integrated Spin Density	nonzero, the same magnitude	zero	zero	non-zero
2*Integrated |Spin Density|	nonzero, the same magnitude	zero	non-zero	non-zero larger magnitude

GdPrCo17	Density (g/cm3)	Lattice Parameter (Angstrom)	Magnetization (Amperes*meter^2 per kg)
CASTEP	8.37	a=b=8.46, c=12.47	158
VASP	8.82	a=b=8.35, c=12.17	110
Experiment	8.46	a=b=8.41, c=12.23	93

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!