First Principles Assessment Materials for Direct Energy Conversion

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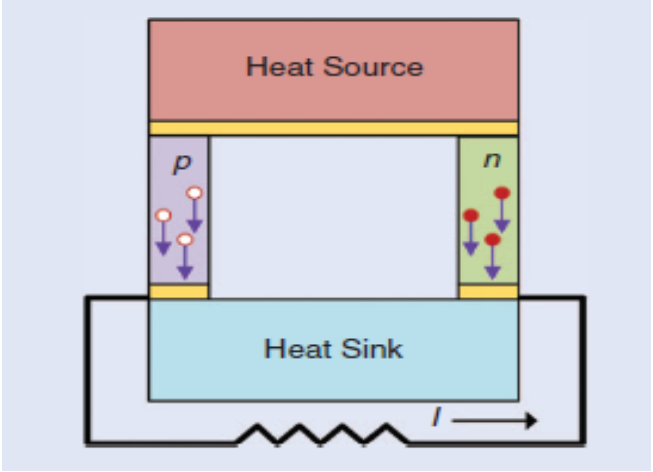
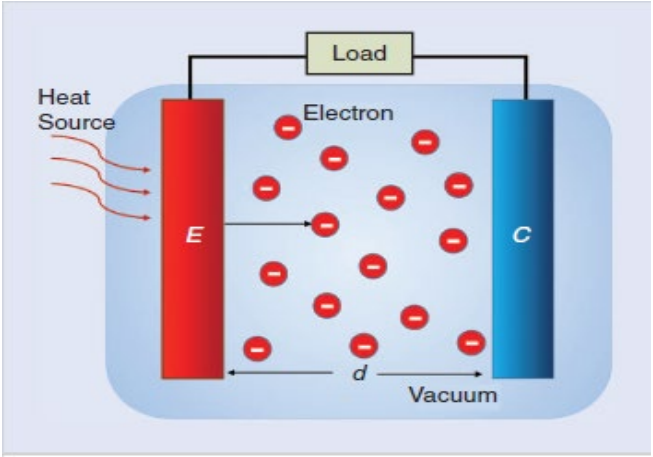
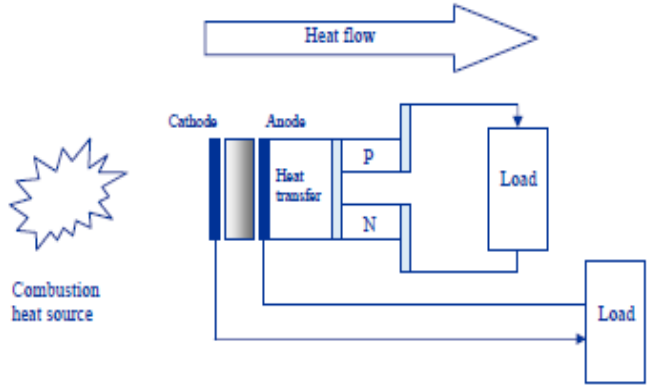
Concept Overview

- Solid state energy harvesting heat from gas turbine engine or radioisotope decay sources offers potential for thermal to electrical energy conversion for aeronautical and space applications.
- Thermoelectric and thermionic material advances offer new opportunities for greater efficiencies.
- Combined they have potential of highly efficient conversion ~ 50%







Characteristics for a desirable thermoelectric material

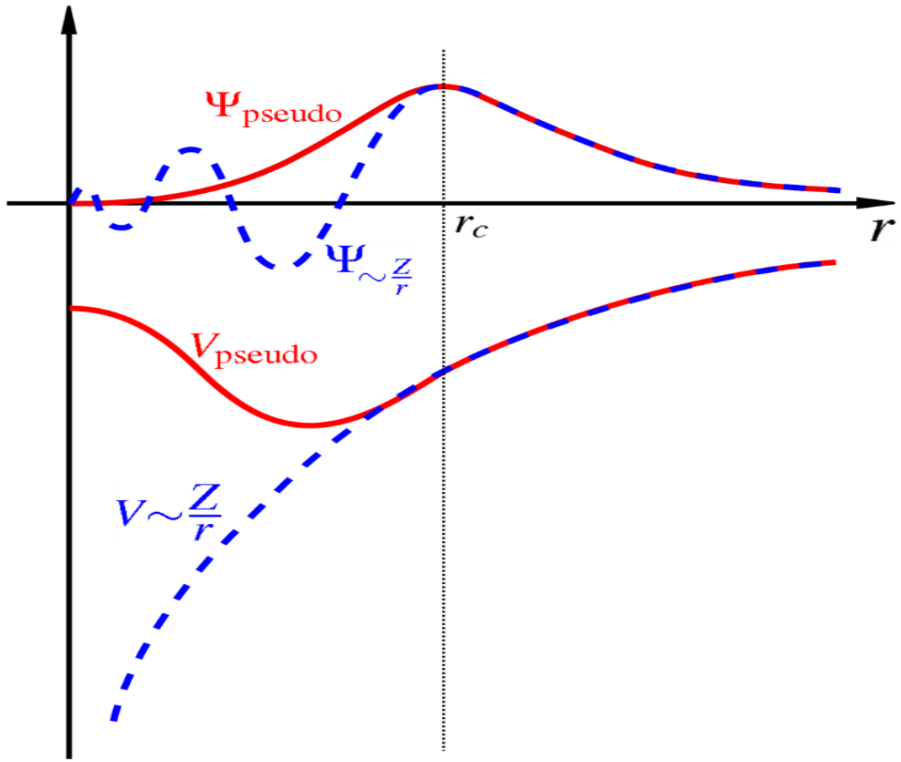
- Seebeck Coefficient ~ 100uV/K
- Electrical Resistivity 10^{-2} Ohm*cm
- Thermal Conductivity ~ 1.0 W/m*K
- Electronic Band Gap -must be greater than zero
- High Temperature Capability

Computational Basis

Kohn–Sham Equation

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x)$$

Hamiltonian operator — Wave function — Energy



Computing Methods

- **Materials Design -MedeA V**ienna **A**b-initio **S**imulation **P**ackage **(** better known as **VASP)**,

- **BIOVIA-Materials Studio- 6. CA**mbridge **S**erial **T**otal **E**nergy **P**ackage (better known as **CASTEP)**

- **Quantum ESPRESSO opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization**.

Complex Oxide – Based Pyrochlore $A_2B_2O_7$

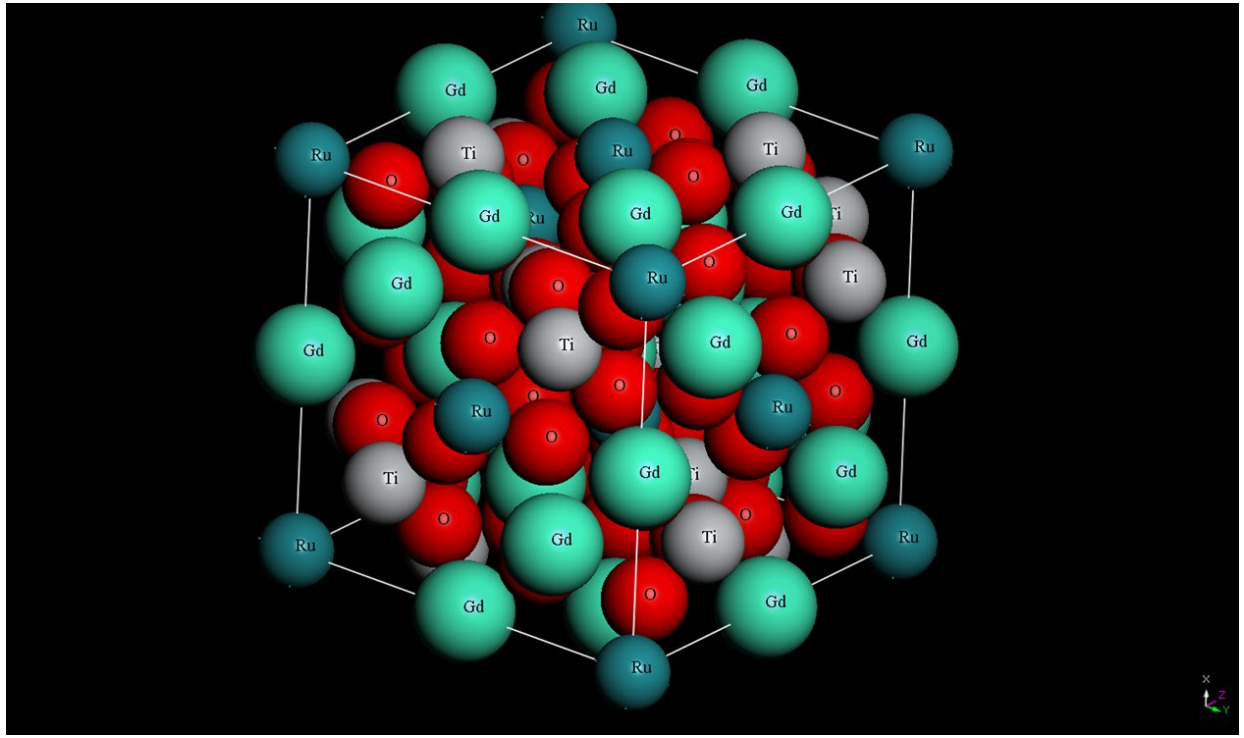
Gd_2RuTiO_7:

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

Gd_2RuTiO_7

Crystal Structure

- Space group: FD-3M
- Gd, Ru, and Ti: chains || x- and y-axis
- Two types of Gd atoms
- O atoms at center of metal tetrahedra
- Octahedral coordination of metal atoms

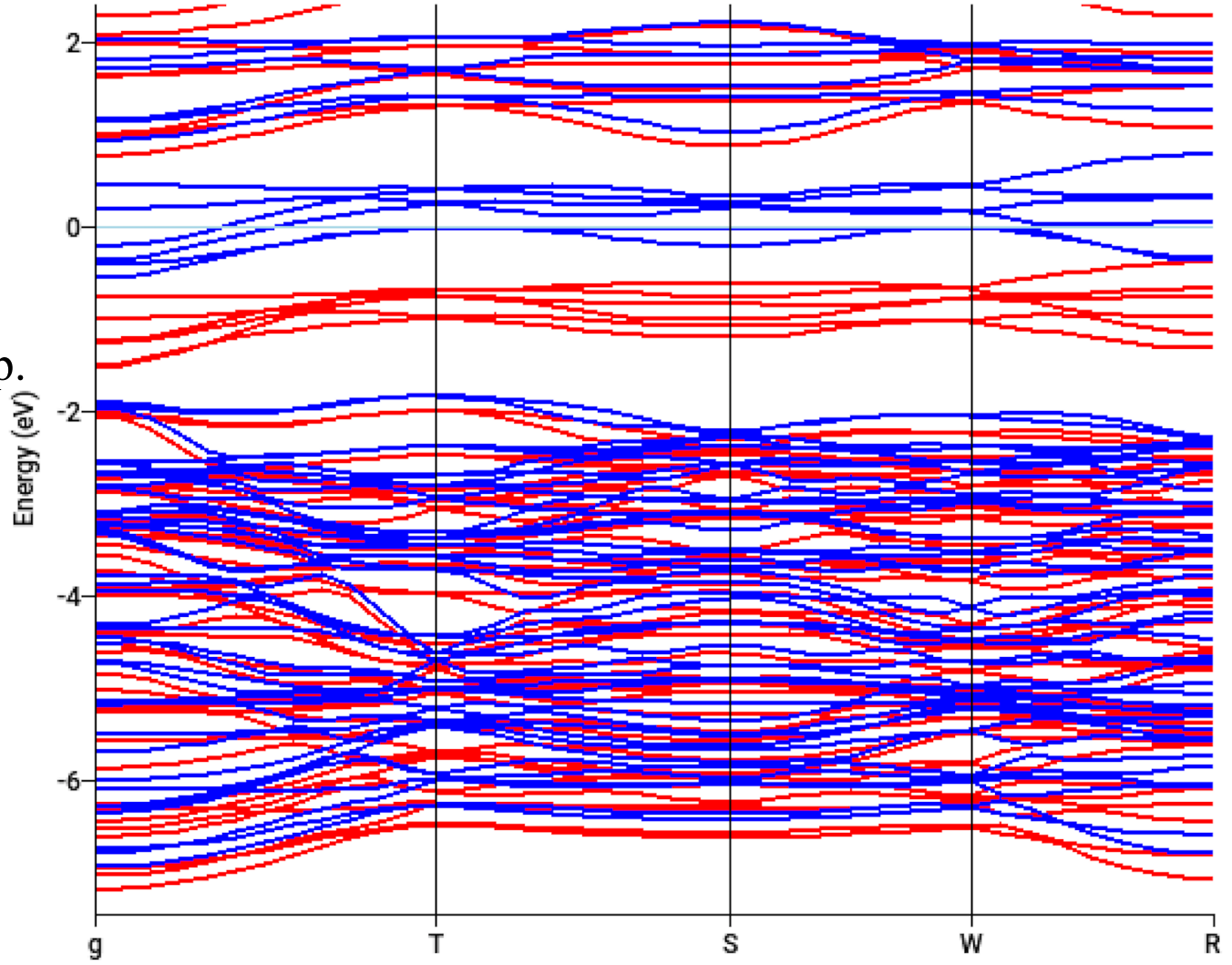


Cell parameters (units Ang)

Parameter	Original	Change	Final	% Change
a	7.239	0.009196	7.248	0.1
b	7.191	0.027895	7.219	0.4
c	7.239	0.009196	7.248	0.1
alpha	60.218	-0.086097	60.132	-0.1
beta	60.610	-0.318938	60.291	-0.5
gamma	60.218	-0.086097	60.132	-0.1

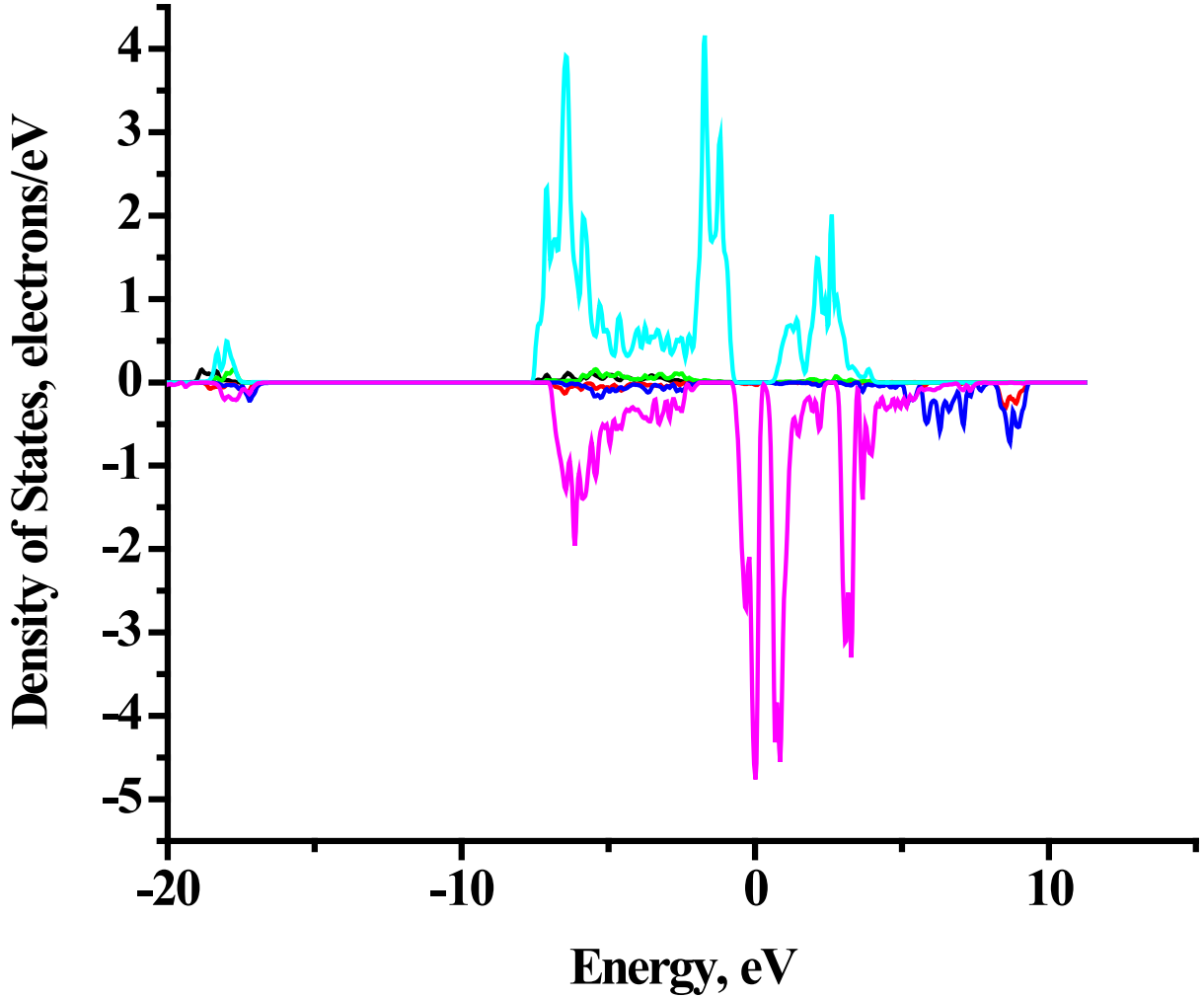
Calculated Electronic Band Structure: Gd_2RuTiO_7

- Half-metallic ferromagnet (like, e.g. CrO_2).
- Ru 4d bands establish the Fermi level and band gap.
- Hybridized Ru 4d + O 2p Orbitals.



Calculated Electronic Partial Density of States

- Ruthenium [Kr] $4d^7\ 5s^1$
- Bands for spin “down” are metallic.
- Bands for spin “up” are semiconducting.
- Indirect band gap of 0.9 eV.



Metric of Thermoelectric Performance

ZT – Dimensionless number of
how good a material functions as a thermoelectric.
(ZT ~ 0.1 to 2.0)

$$\mathbf{ZT} = \frac{\boldsymbol{S^2 \sigma T}}{\boldsymbol{\kappa}}$$

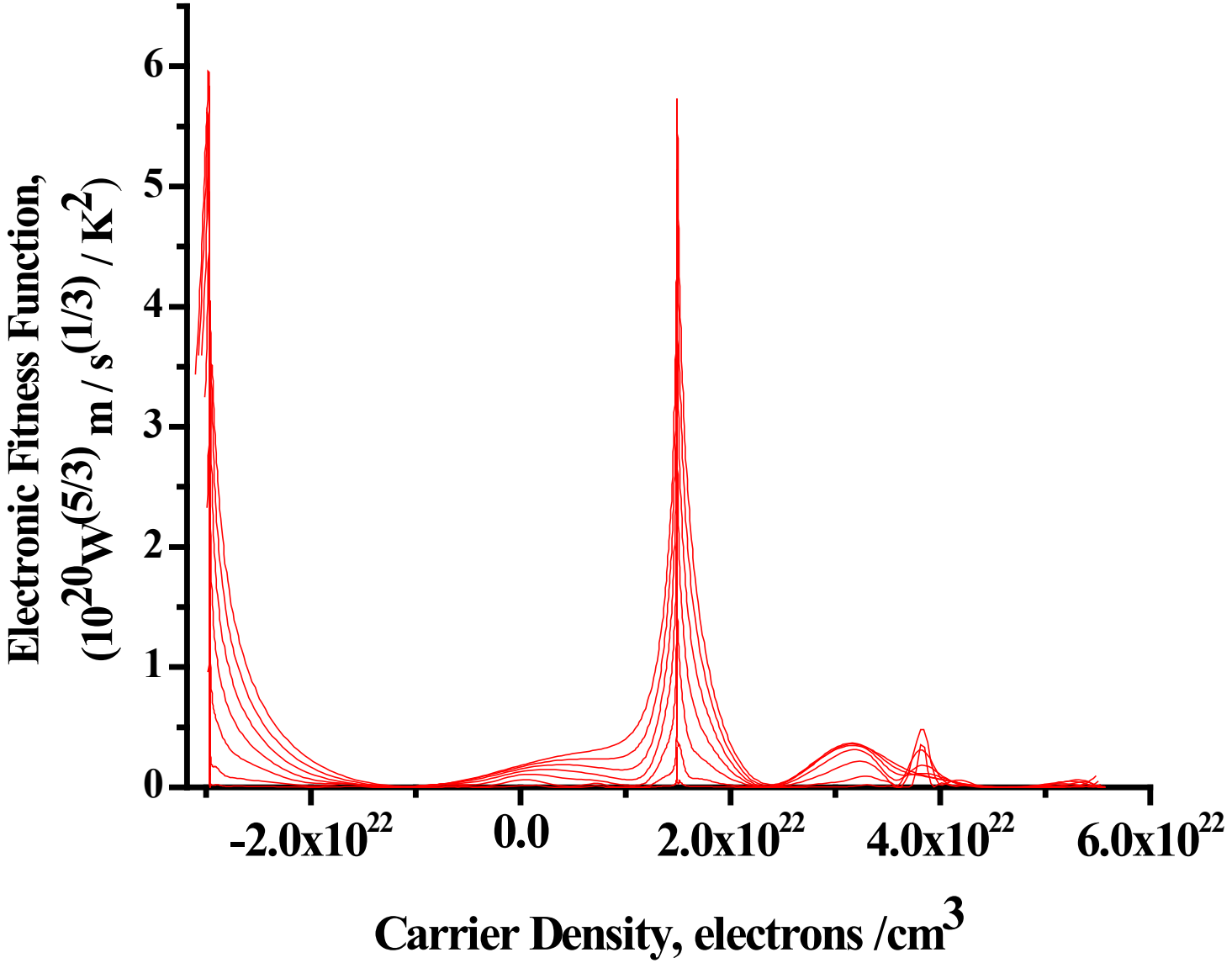
EFF – Electronic Fitness Function describes
electronic aspect of thermoelectric material.

$$\mathbf{EFF} = \frac{\left(\frac{\boldsymbol{\sigma}}{\boldsymbol{\tau}}\right) \boldsymbol{S^2}}{\boldsymbol{N^{\frac{2}{3}}}}$$

Electronic fitness function for screening semiconductors as thermoelectric Materials. *Singh, et.al.* *PHYSICAL REVIEW MATERIALS 1, 065405 (2017)*

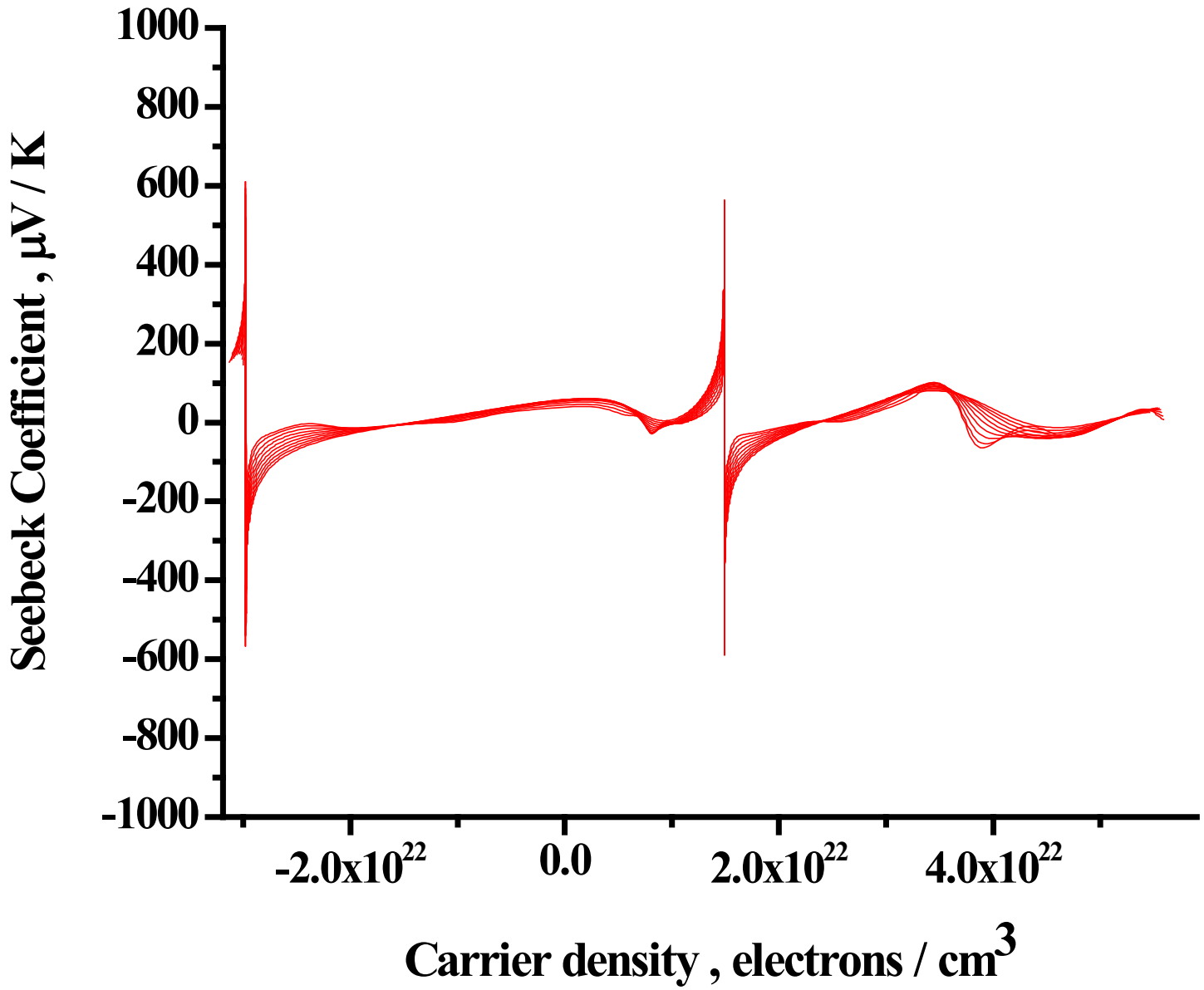
Isothermal Electronic Fitness Functions: Gd_2RuTiO_7

- Gd_2RuTiO_7 may not be a good thermoelectric.
- However dopants may increase performance.
- Injection of either p-holes or n-electrons may improve things.



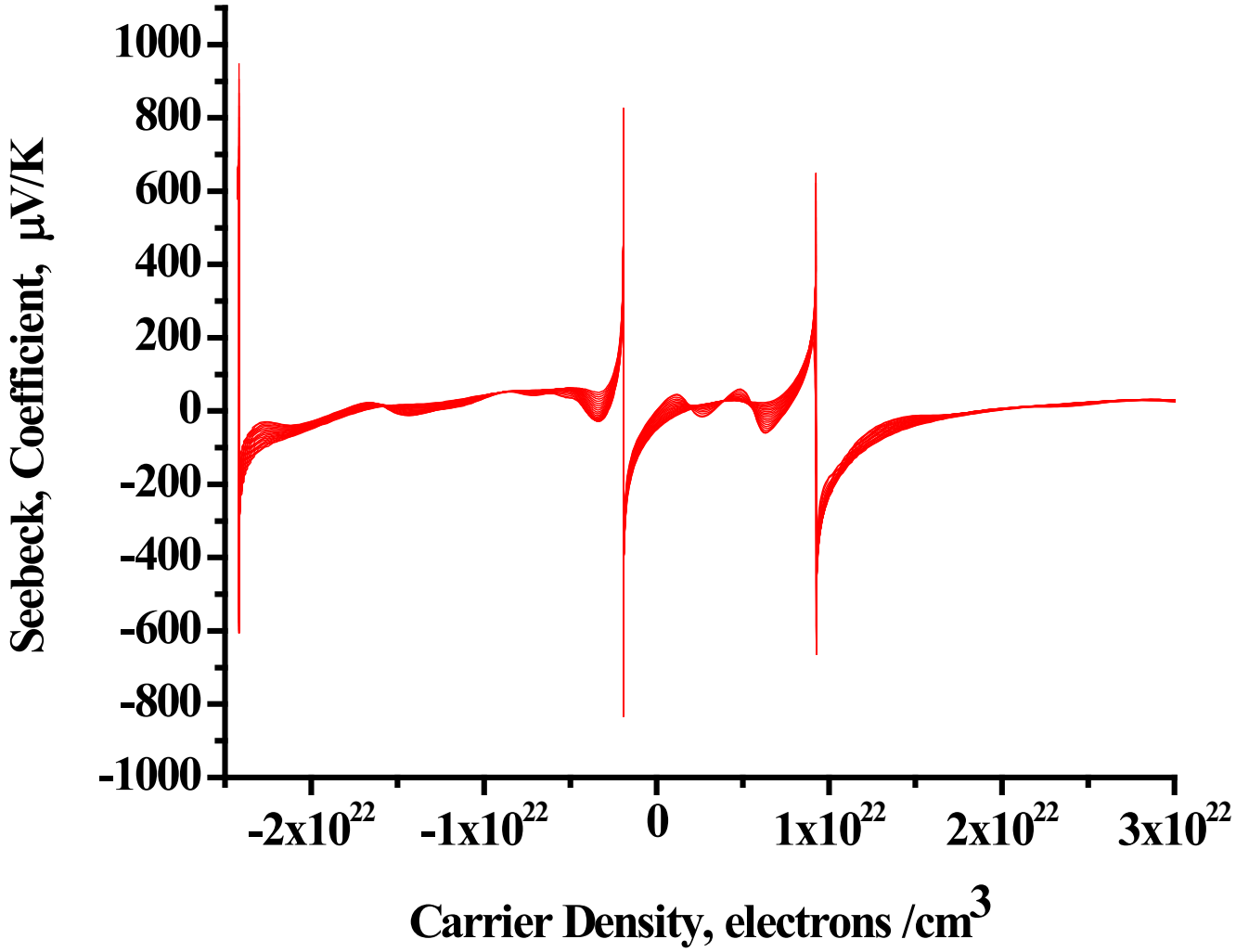
Isothermal Seebeck Coefficient: Gd_2RuTiO_7

- Duality in band structure.
- Possible p-type thermoelectric
- Temperature = [250:650] K

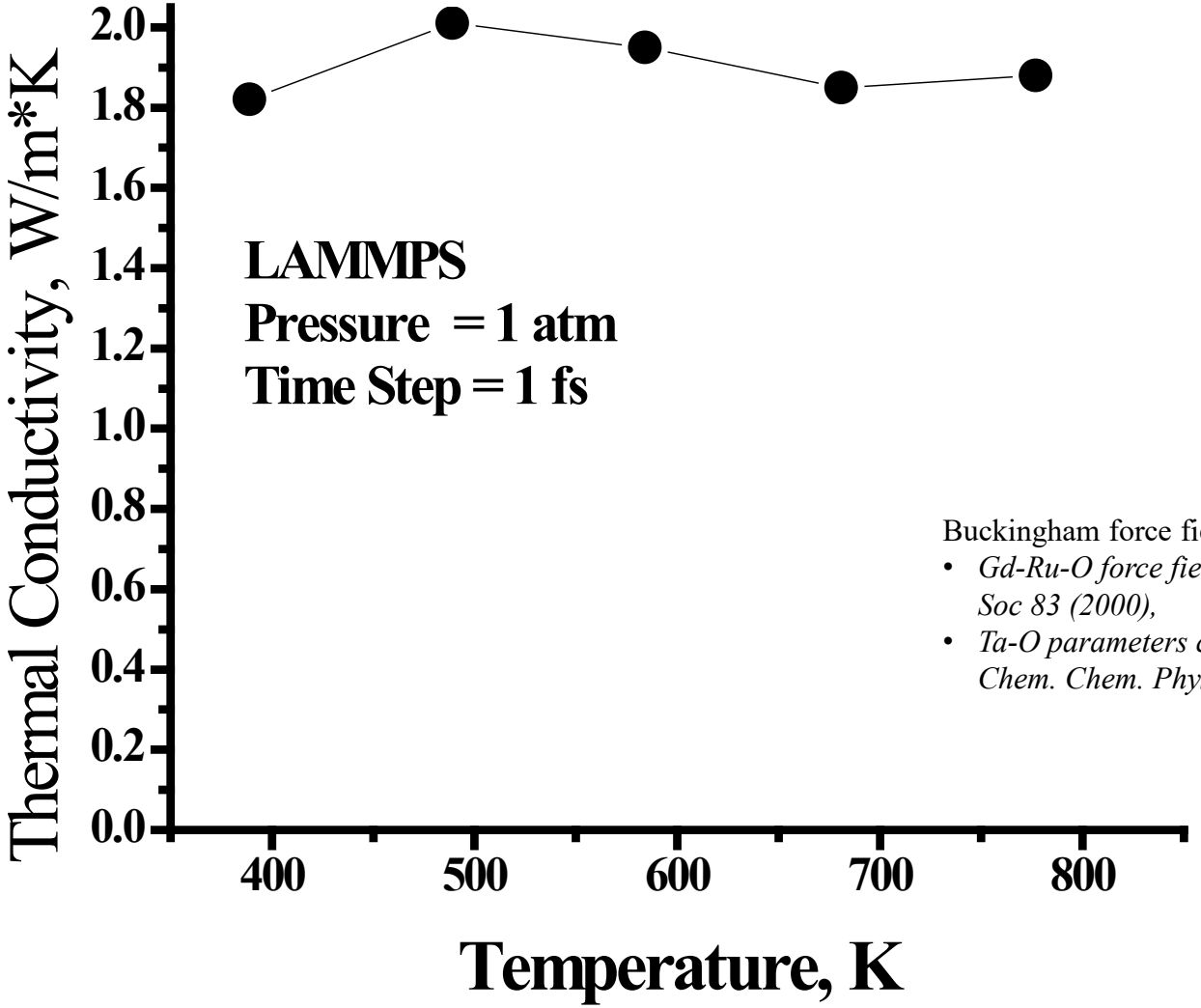


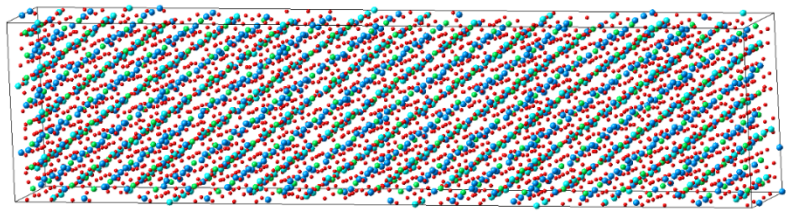
Isothermal Seebeck Coefficient: Gd_2RuNbO_7

- Niobium [Kr] $4d^4 5s^1$
- Possible p-type dopant
- Temperature = [250:650] K



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

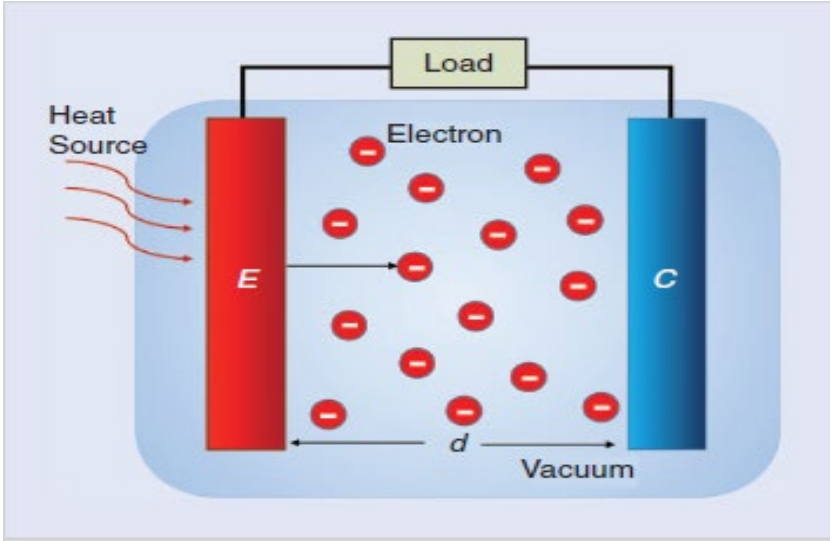




Buckingham force field:

- *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).*

Thermionic Emission



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

Ceramic Emitter: Strontium Vanadate ($SrVO_3$)

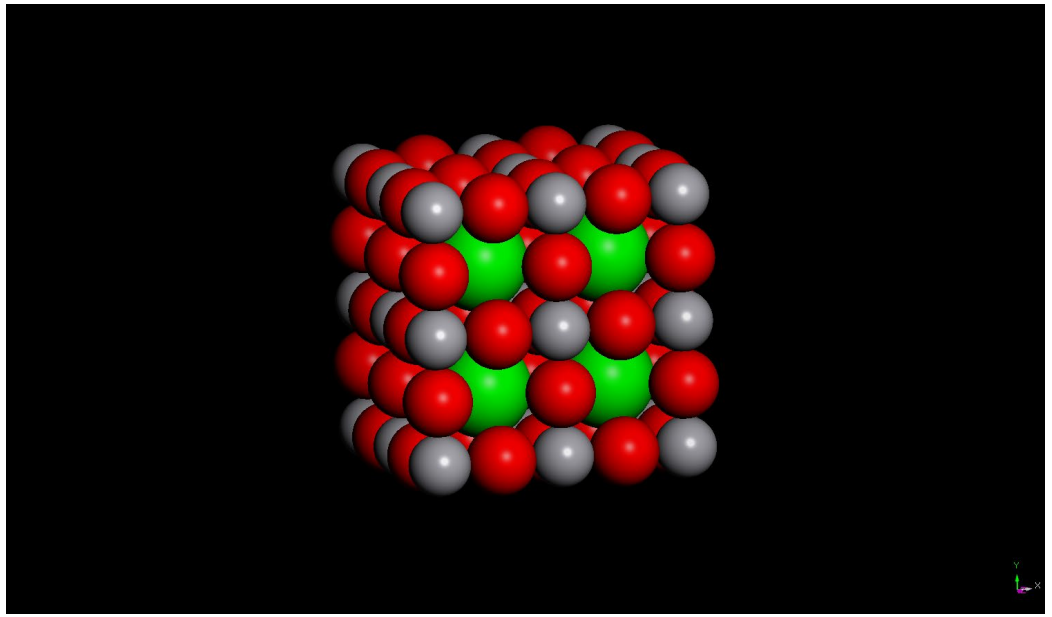
Compound candidate material for emitter synthesis:

Low Intrinsic work function predicted to be 2.609 eV.

Density: 5.449 g/cm^3

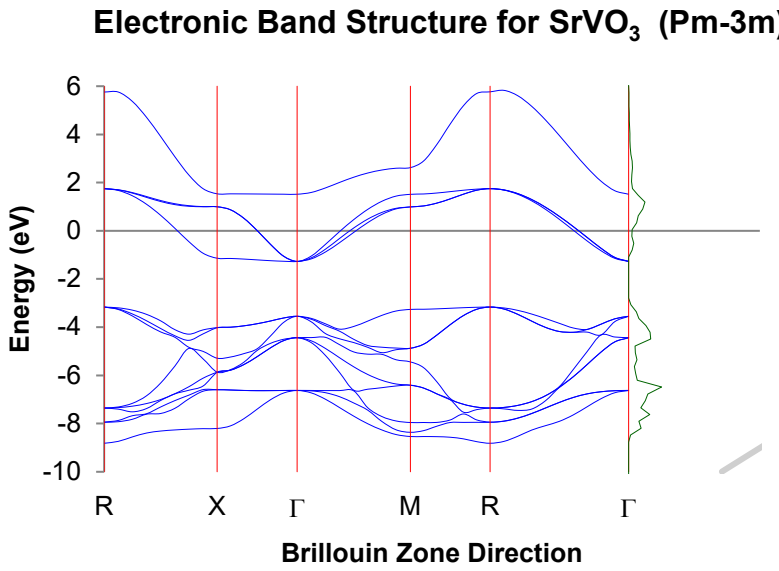
Analysis of the electronic structure:
The system is a metal.

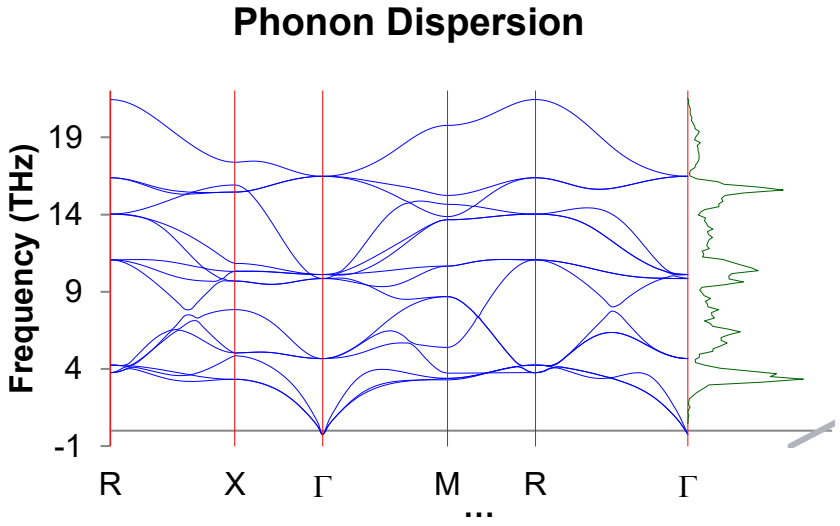
The Fermi energy is located in the band interval (#21 - #25) spanning the energy interval
(-3.870:-1.721)eV with respect to the Fermi level.



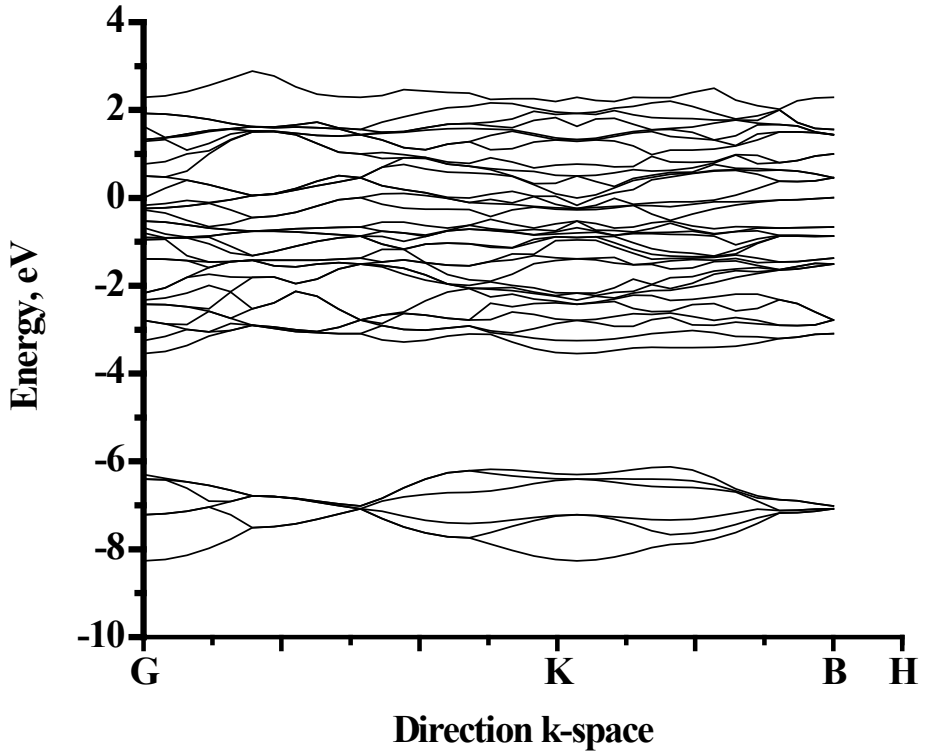
Calculated Electronic and Phonon Characteristics : Strontium Vanadate ($SrVO_3$)

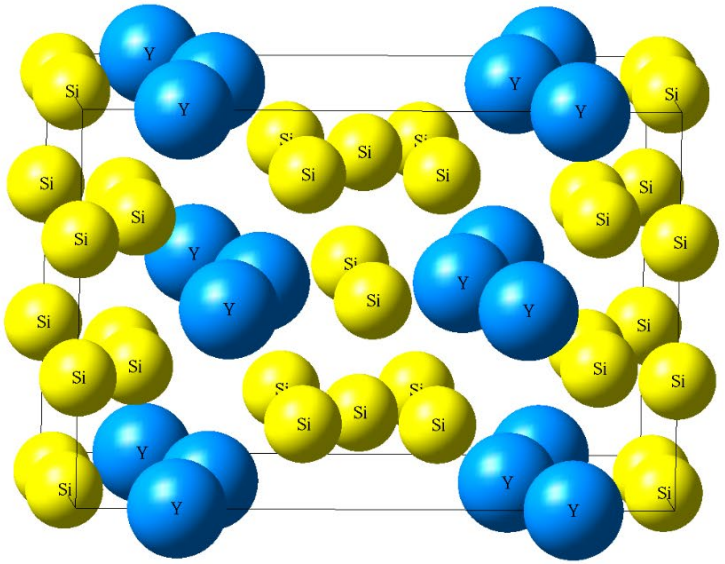
- Electronic band structure which is metallic in nature. Hence a good candidate as an emitter
- Phonon dispersion curves predict stable cubic crystal structure
- Lattice parameter 7.725 Angstroms





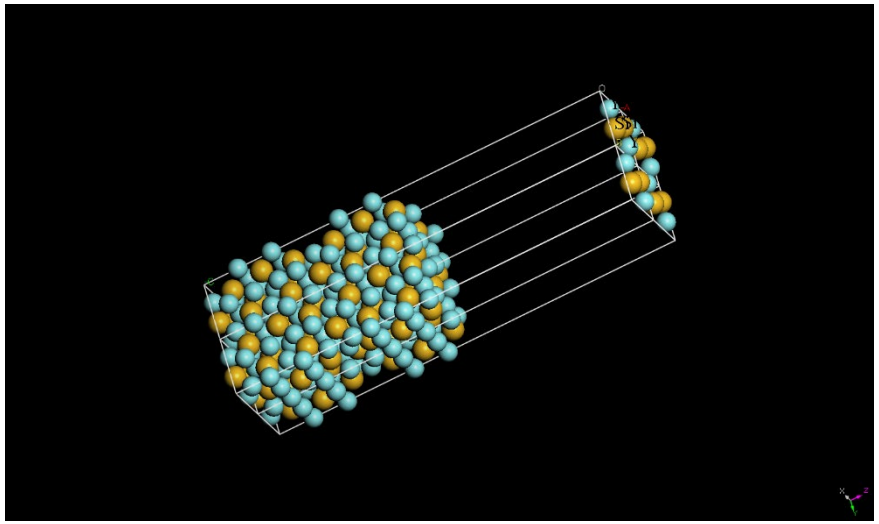
Intermetallic Emitter: Yttrium Trisilicide (YSi_3)



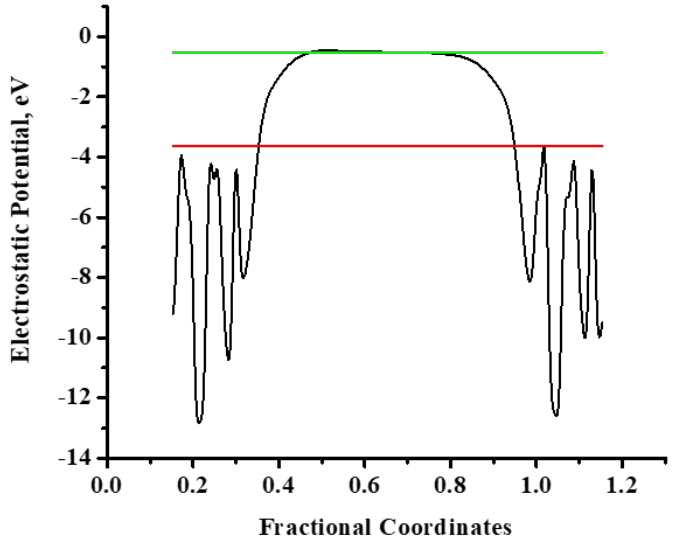


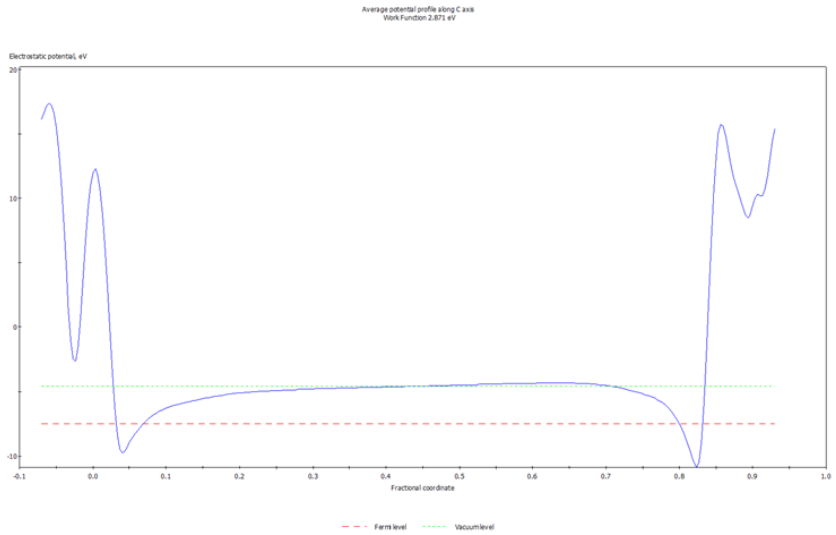
Work Function Calculation: Yttrium Trisilicide (YSi_3)

- Constructed in a slab geometry surface (001) atomic planes separated by a vacuum layer.
- Compare values of the Fermi energy and the electrostatic potential in a vacuum.

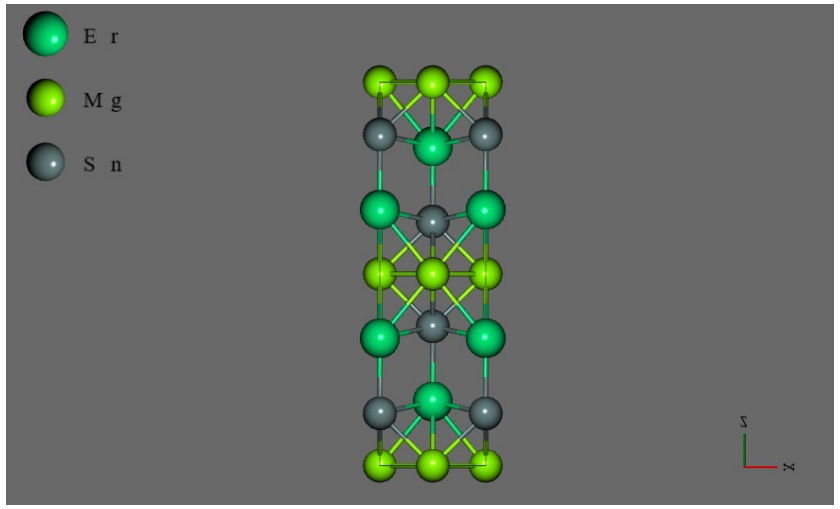


- Addition of 10 % carbon results in a reduction of the work from 3.14 eV to 2.87 eV
- Reduced work function means lower temperature for operation.

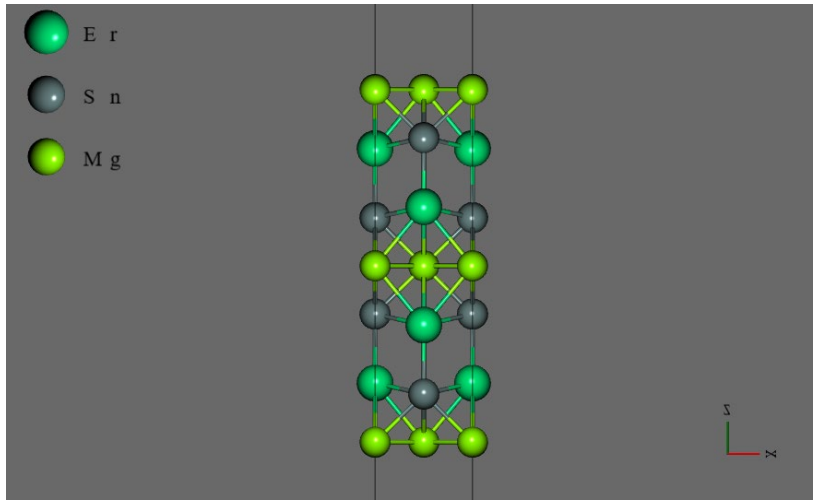




Electride Emitter: Erbium-Magnesium-Tin (ErMgSn)



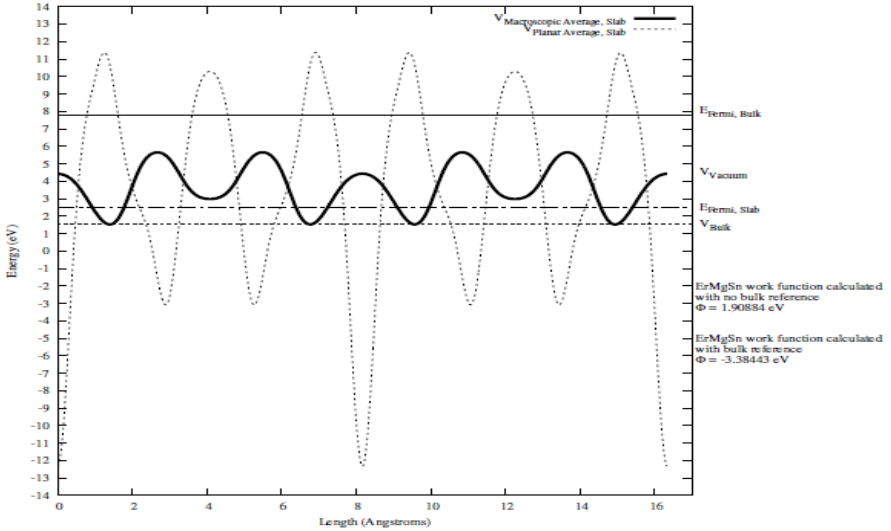
Bulk

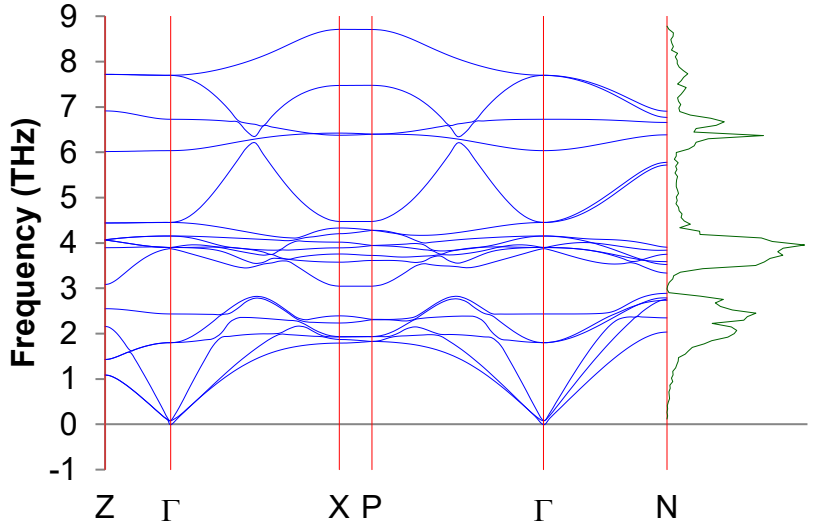


Slab/cleaved surface

Cleaved surface (001) direction with vacuum between the surfaces

Work function prediction: 1.91eV along the z-axis



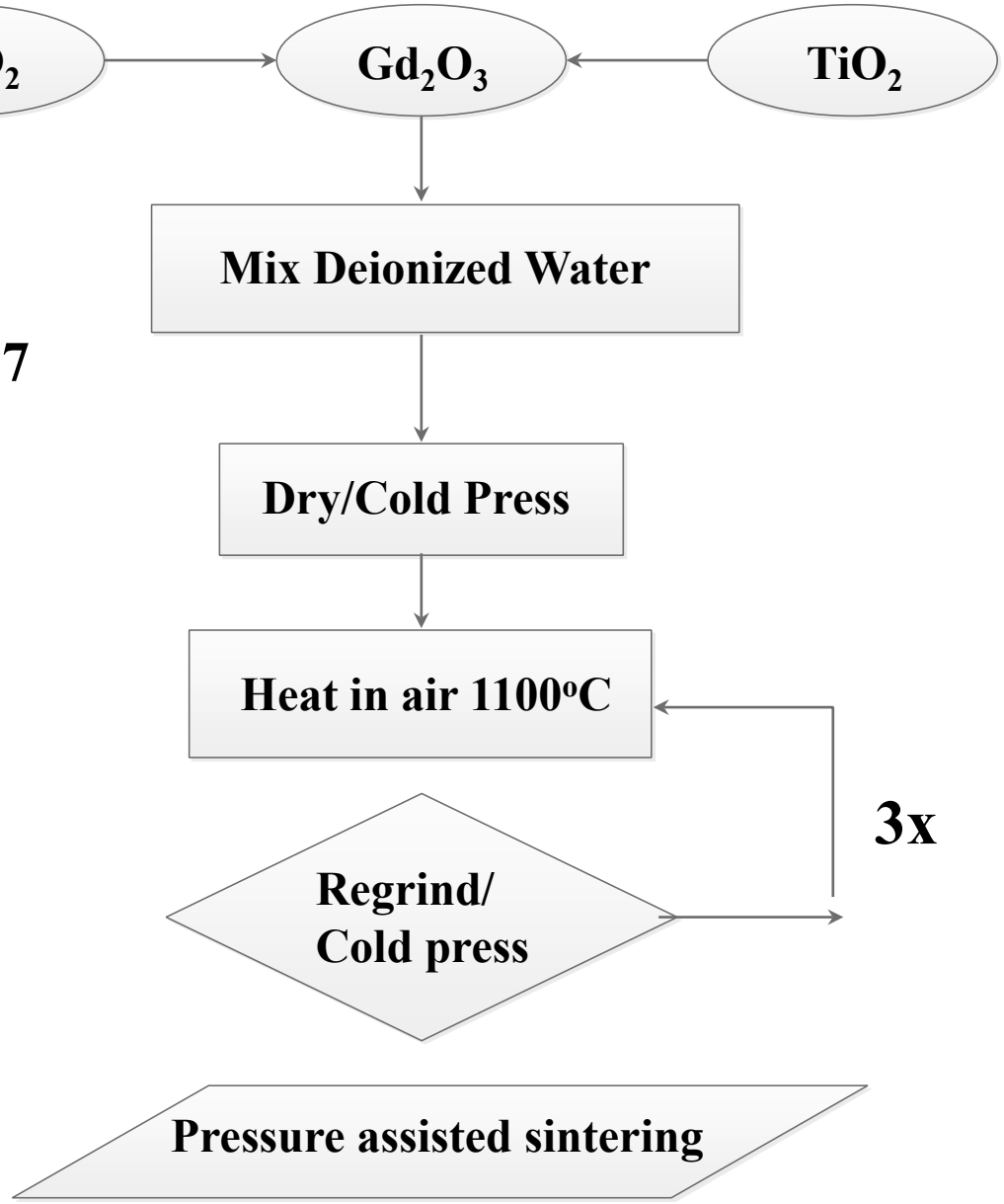


"Discovering Inorganic Electrides from an Automated Computational Screening" (Q. Zhu & T. Frolov, LLNL Report)

Synthesis Route for Oxide Pyrochlore

$$Gd_2O_3 + TiO_2 + RuO_2 \longrightarrow Gd_2RuTiO_7$$

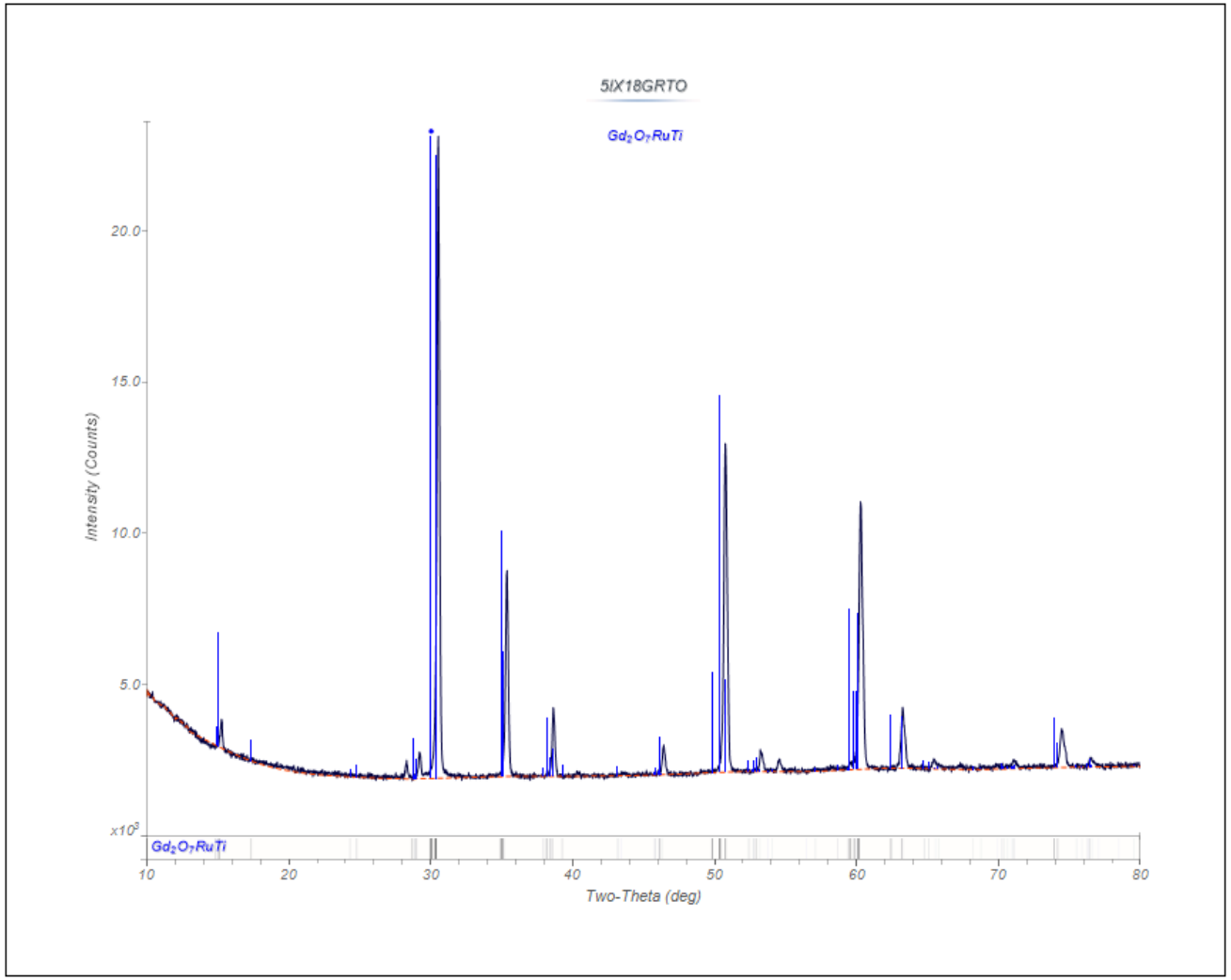
- Solid State diffusion reaction synthesis
- RuO_2 20% above stoichiometry
- Heating anneal times ~ 24 hours
- Pressure assisted sintering at 900°C and 9KSI



Comparison Between Calculated and Experimental XRD: Gd_2 $RuTiO_7$

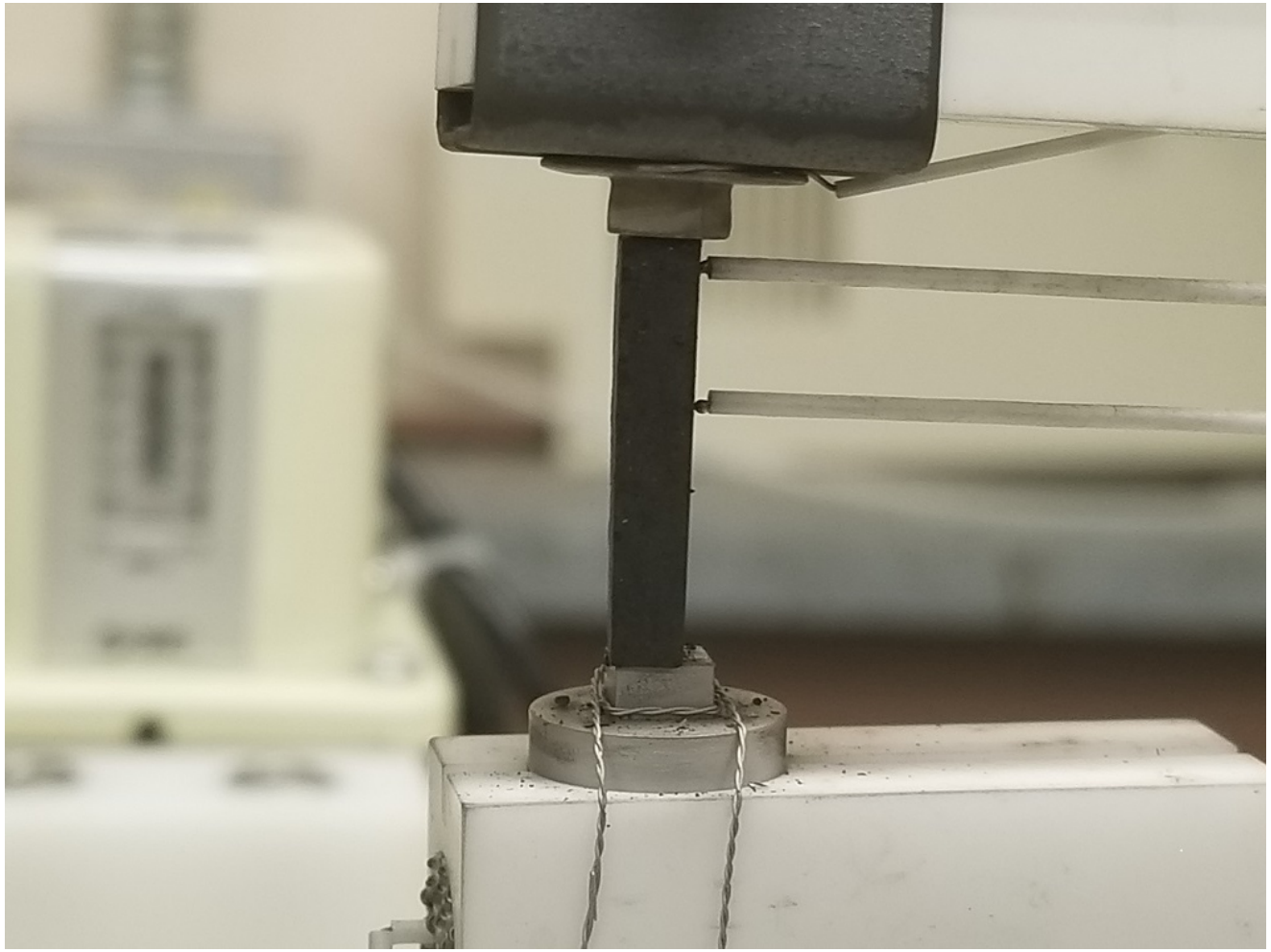
Comparison of the optimized geometric Structure with experimental XRD

Crystallographic Information File (CIF) results imported into XRD MDI JADE



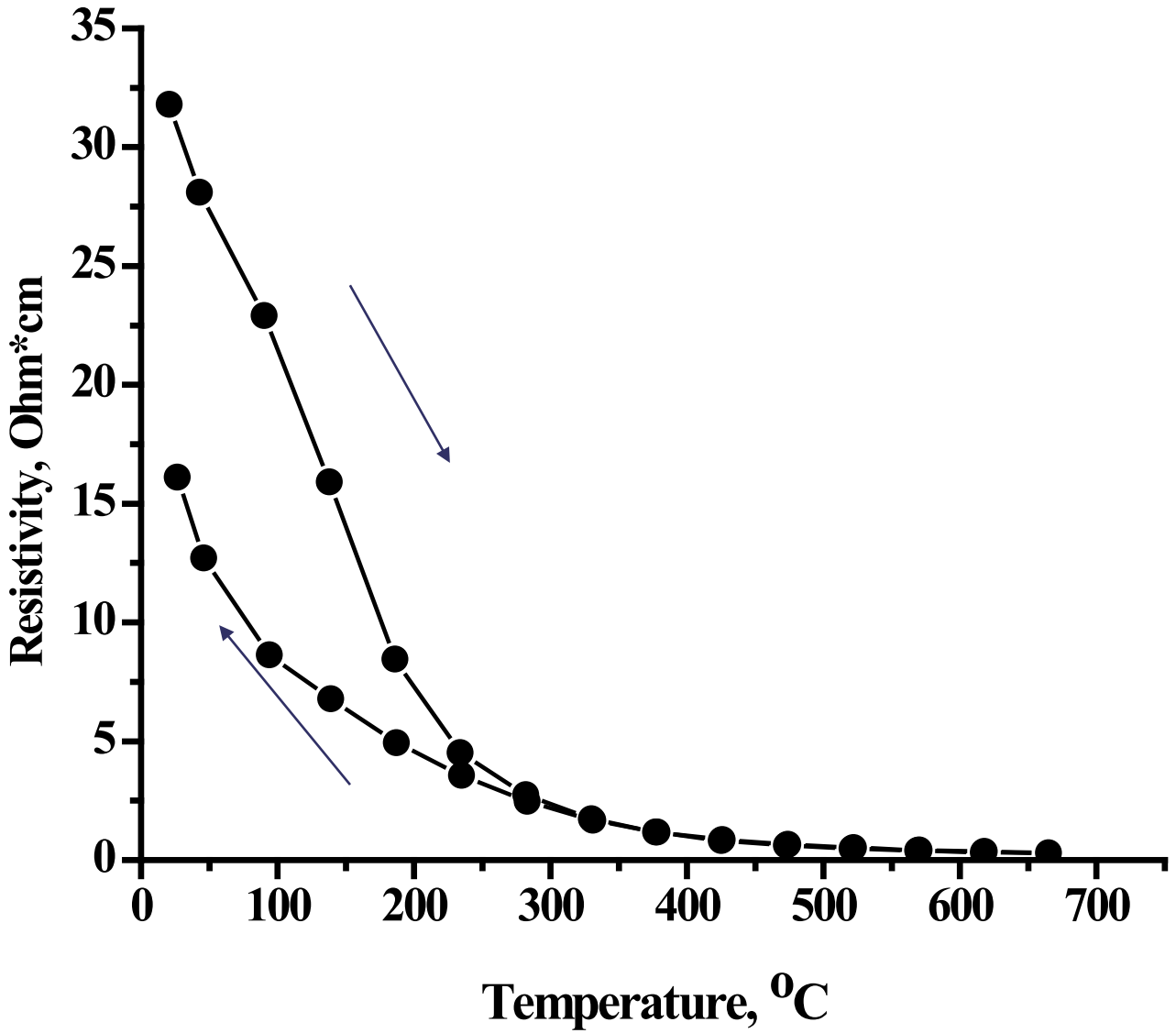
Electronic Property Measurements: $Gd_2 RuTiO_7$

- **Seebeck Coefficient/ Electric Resistance measurement**
- **Model ZEM-3 ULVAC- Riko Inc. Japan**
- **Sample length 19 mm**



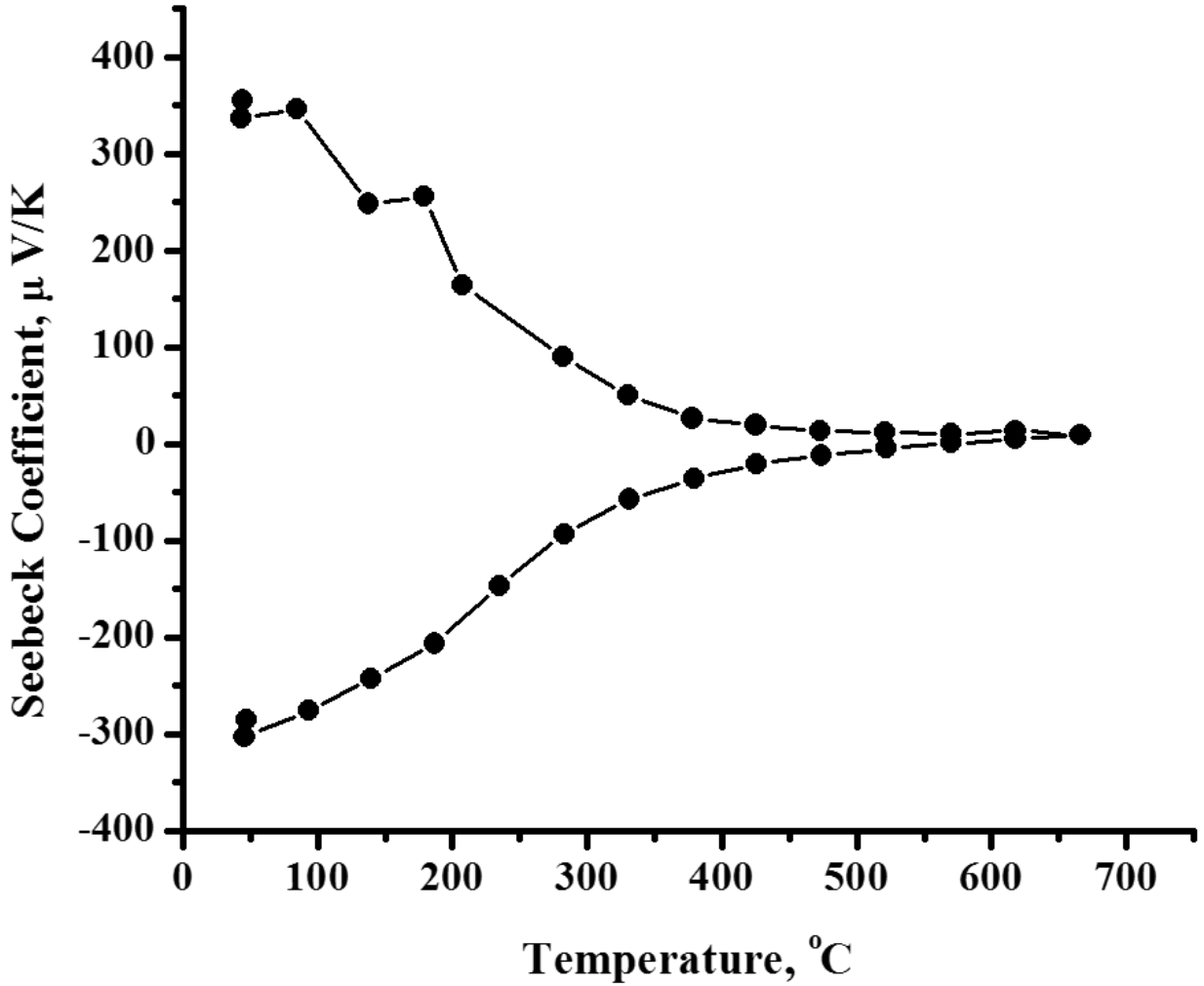
Electronic Property Measurements: $Gd_2 RuTiO_7$

- **Electrical resistivity decreases with temperature.**
- **Characteristic semiconductor behavior.**
- **Hysteresis indicates possible difference in carrier concentration.**



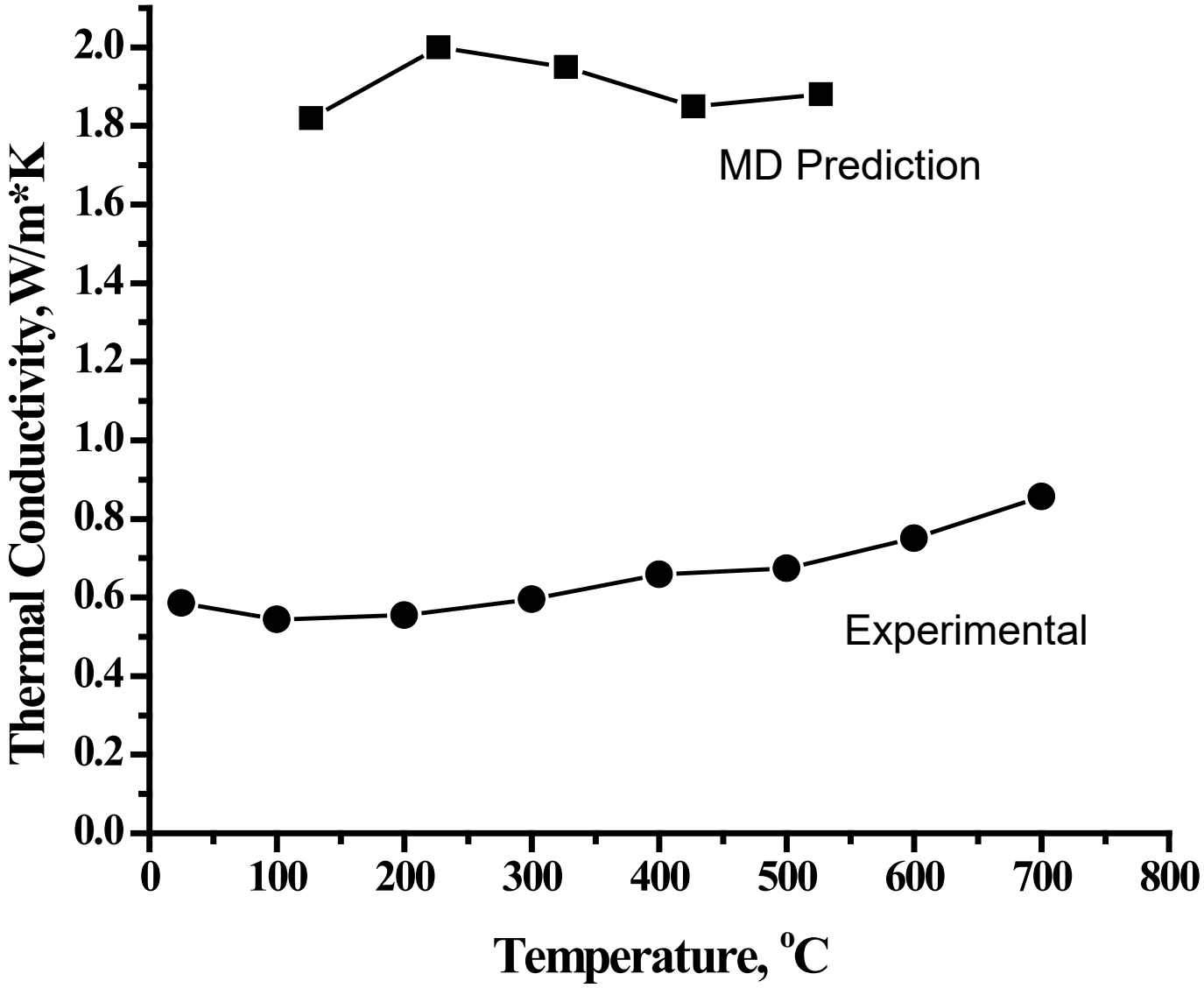
Electronic Property Measurements: $Gd_2 RuTiO_7$

- Seebeck coefficient decreases with increasing temperature.
- Initially p-type behavior.
- Decreasing temperature the material exhibits n- type behavior.



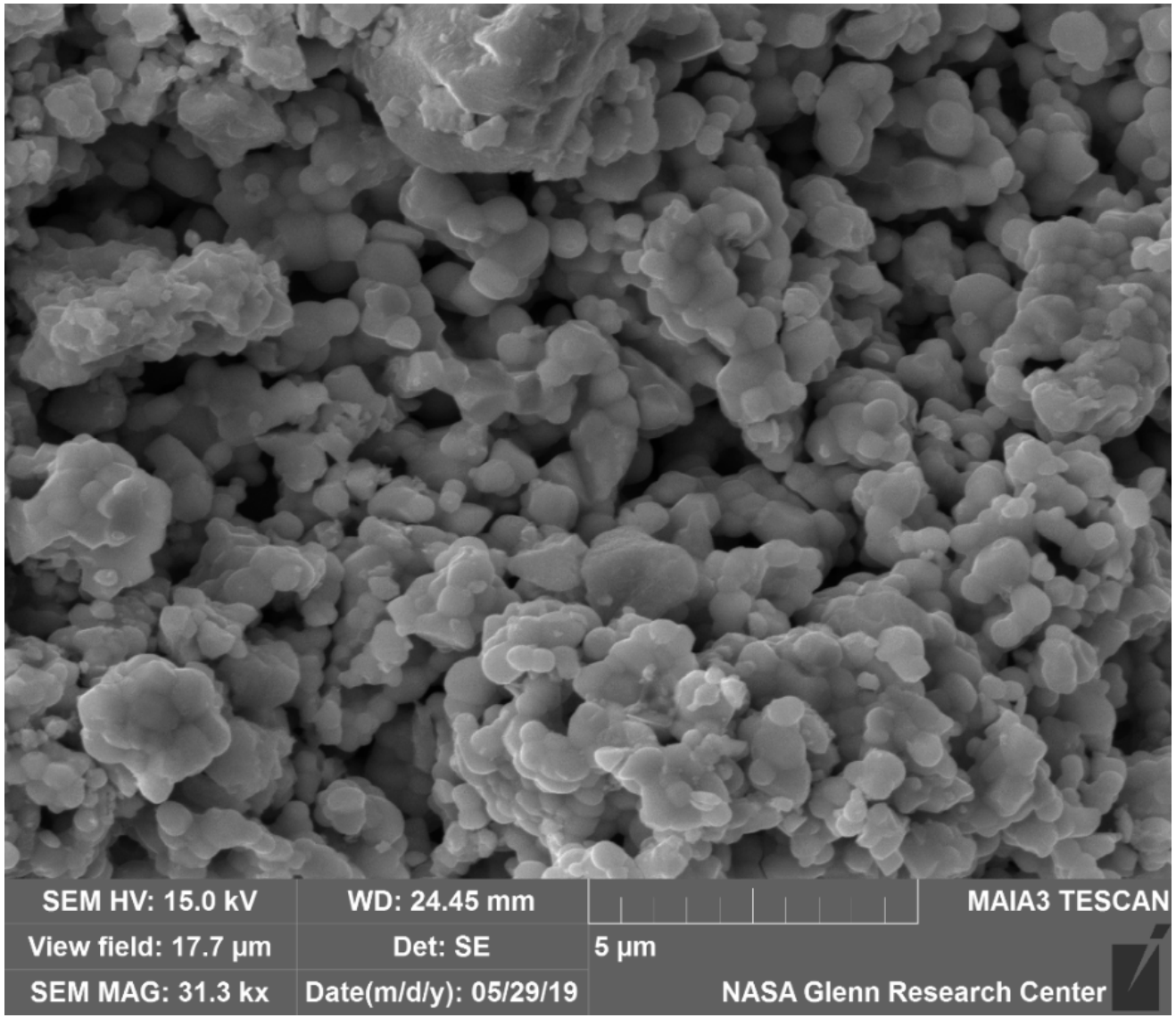
Thermal Property Measurements: Gd_2RuTiO_7

- Thermal conductivity obtained with LASER flash method.
- Netzsch model LFA 467 Hyper Flash
- Lower than predicted thermal conductivity
- Behavior not predicted with MD.

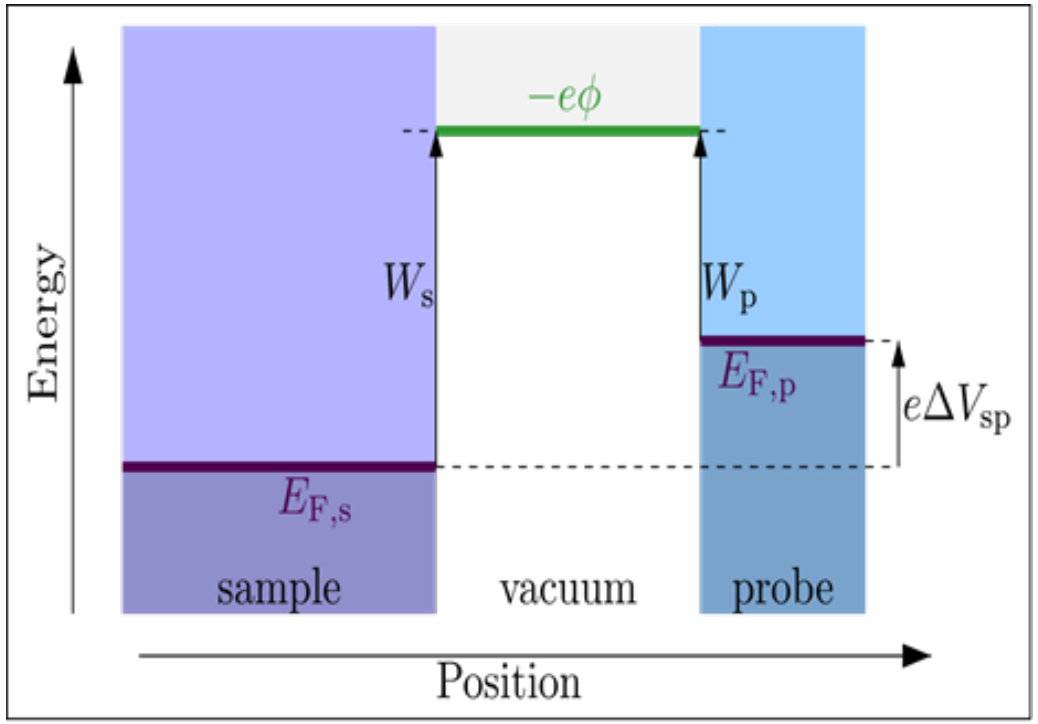


Scanning Electron Micrograph of $Gd_2 RuTiO_7$

- Electrical and thermal response due in part to porosity.
- DFT predicts 7.096 g/cm^3 while the measured value is 3.452 g/cm^3
- Only 50 % of full density.



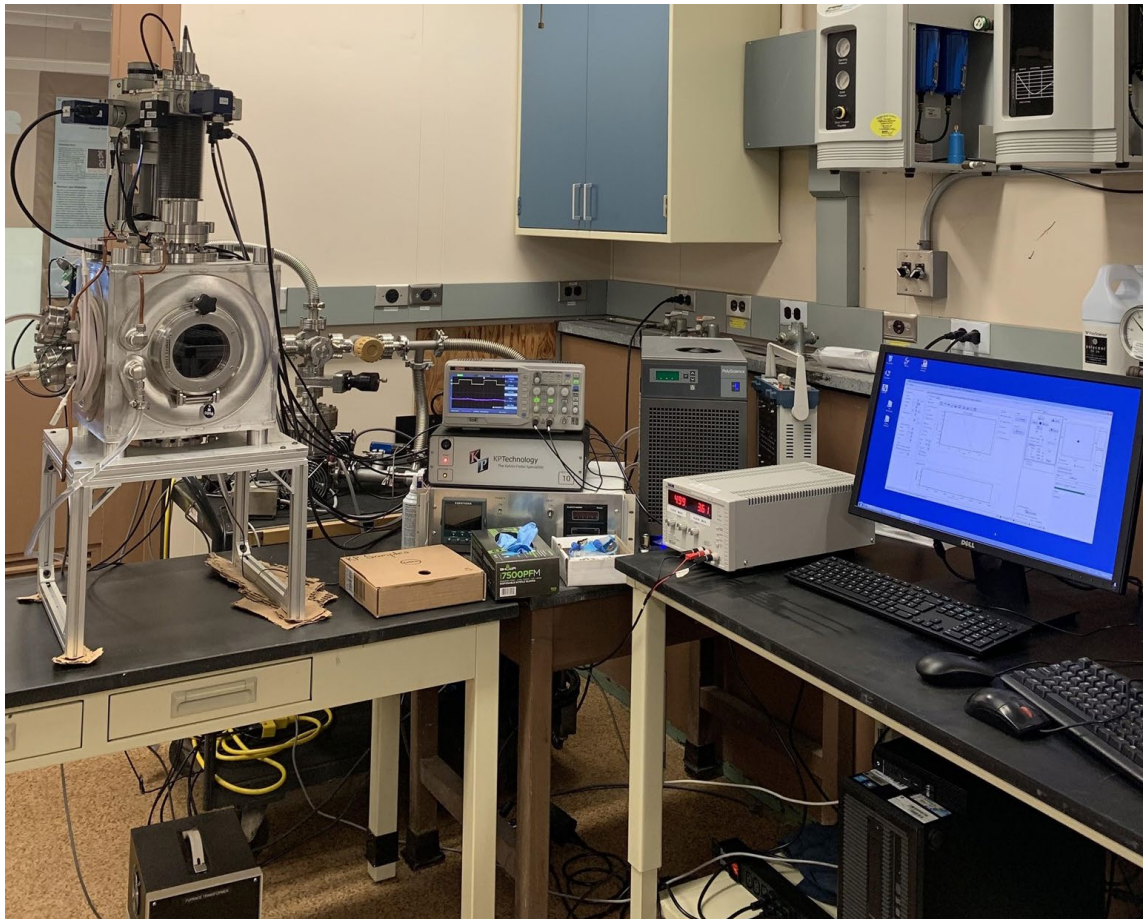
Work Function Measurements



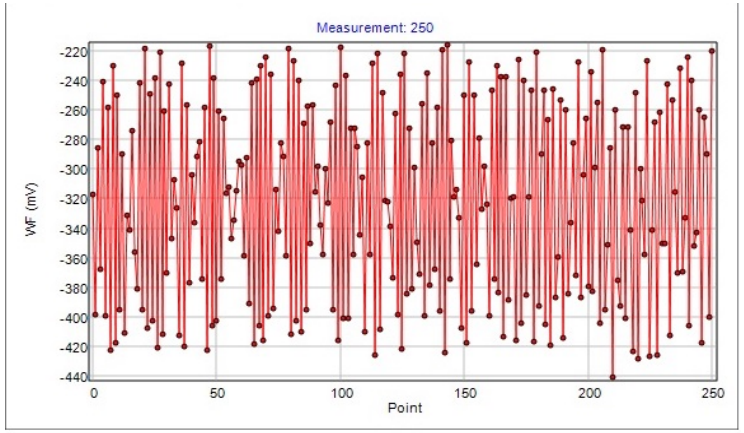
$$e\triangle V_{sp} = W_s\text{-}W_p$$

- The Kelvin Probe Method measures the Contact Potential Difference (CPD) between a sample and a tip.
- Vibrating the tip above the sample, and measuring the varying capacitance of the system using a backing potential.
- The CPD may then be used to calculate the work function of the sample by calibrating the system using a material with a known work function like gold.

Ultra-High Vacuum Kelvin Probe



Single point measurement of Gold

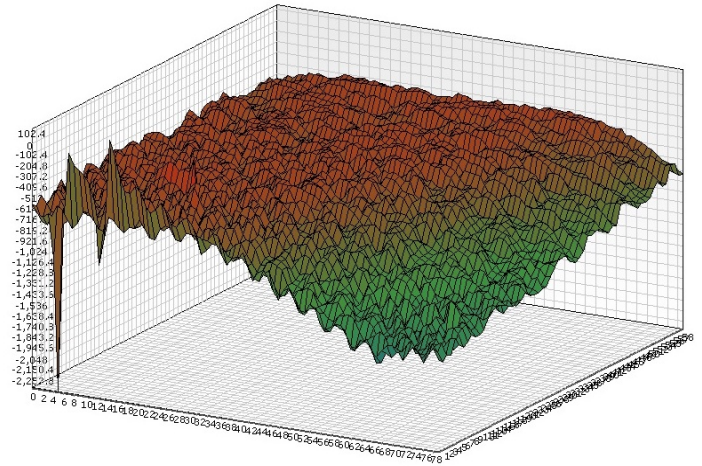


Point	WF	WF(RA)	GD	Height(um)	User	Time (sec)
250	-220.5	-303.4	308.4	0.0	0.0	271.300

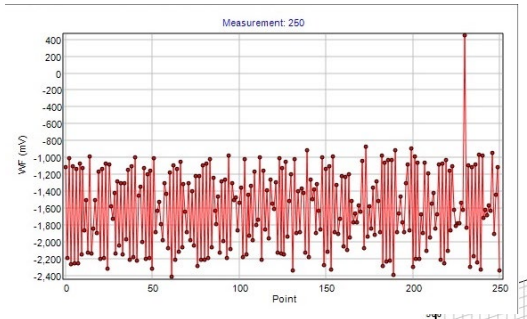
Mean WF (mV) = -323.4 Std = 67.5

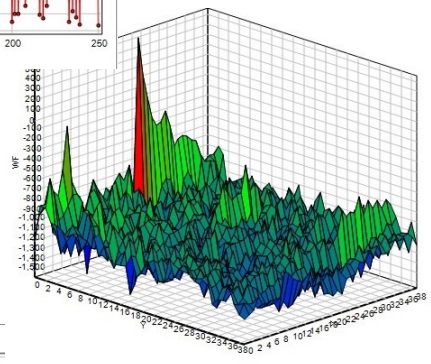
Mean GD (au) = 308.0 Std = 3.1

Scan of Gold / Aluminum

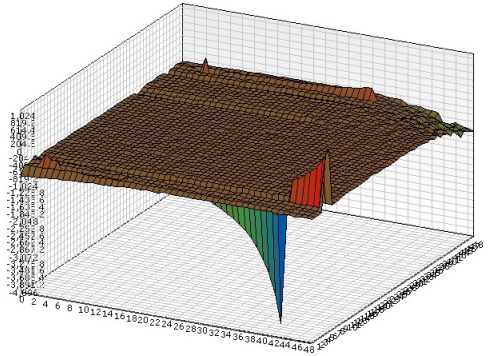


Work Function Measurements

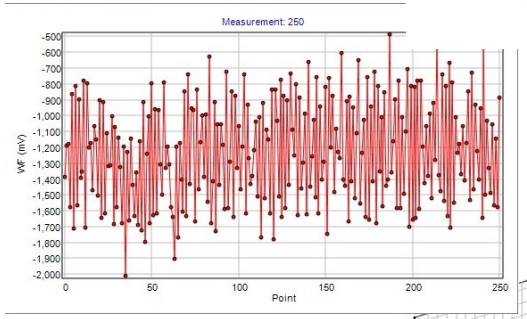


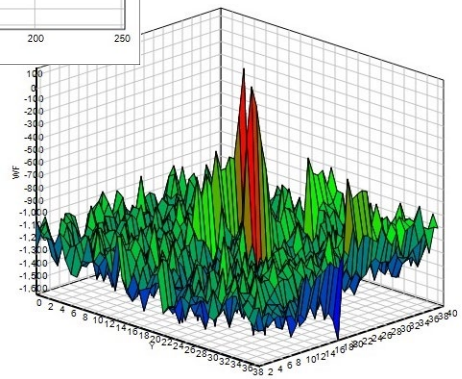


Work Function: 3.51 eV
DFT result 3.14 eV

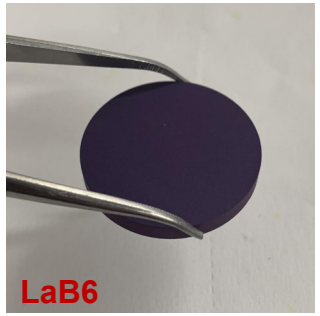


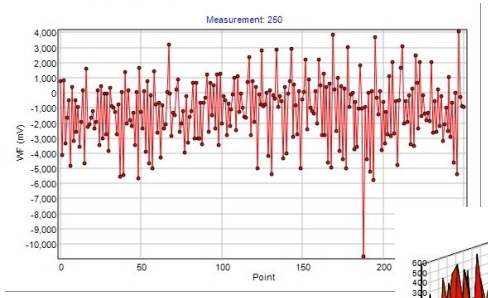
Work Function: 4.61 eV
Literature: 4.83 eV [Allen & Gobeli, 1962]

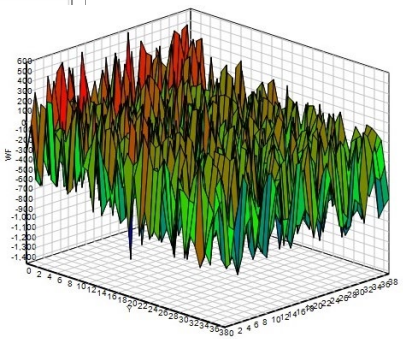




Work Function: 3.88 eV
Literature: 3.0 eV - 4.67 eV [Fomenko, 1994]







Work Function: 4.72 eV
Literature: 4.84 eV [Zimmer et al., 2011]

Conclusions

- **Computational methods parameters can be used for predictions and to aid in the development of thermoelectric and thermionic materials.**
- **DFT- is only a guide processing is equally important.**
- **Nature is always right!**