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Combined computational and experimental study of zirconium tungstate

Eunja Kim (UNLV)
Margaret E. Gordon (SNL), Philippe F. Weck (SNL), Jeffery A. Greathouse (SNL), Stephen P. Meserole (SNL), Mark Rodriguez (SNL), Clay Payne (SNL), Charles R. Bryan (SNL)

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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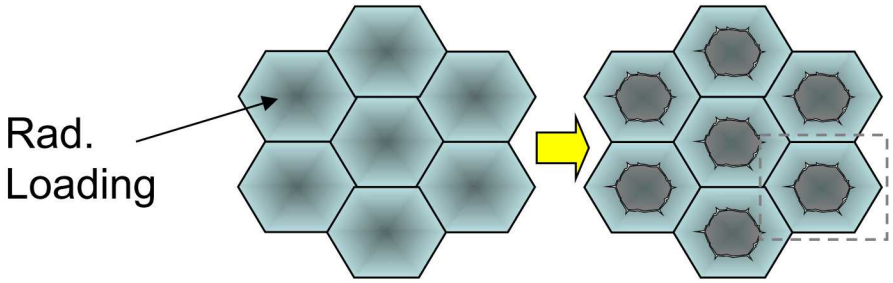
Nuclear waste forms

- Radioactive materials:
  - 34 tons of weapons-grade Pu metal from the US weapons program
  - *Long-lived isotope of technetium*, ^{99}Tc ($t_{1/2}$ = 2.1 x 10^5 years, β^-= 0.294 MeV; 6% of the fission yield for ^{235}U)
- C*hemical and physical waste forms for immobilizing* radionuclides (e.g., U, Pu, Tc):
  - Pu-waste form to isolate the radionuclides for extended periods of time needed
  - No effective Tc waste form identified yet (e.g., *highly mobile* as soluble TcO_4^-, volatile at elevated temperatures such as vitrification)
- Ideal radioactive material waste forms:
  - Low solubility
  - Ability to isolate radionuclides from the environment for long periods of time
  - Resistant to radiation damage that can lead to expansion, crumbling, increased exposed surface area, thus more rapid dissolution
- Ceramic waste forms (e.g., Zr-W-O and/or Zr-W-P-O).

Ceramic waste forms: ZrW_2O_8

- Negative thermal expansion (NTE)
  - Contract upon heating
  - Naturally–occurring Zr minerals
  - Readily incorporate radionuclides (e.g., U, Tc, Pu) through substitution
- Radiation induced amorphization
- Zoned waste forms
  - No pressure exerted on the shell
  - No rupture of individual grains, mitigating the effect of amorphization on radionuclide release
  - Easy to maintain isolation of the radionuclide for long periods of time

Good candidate for radiation resistant waste forms!



Combined computational-experimental strategy

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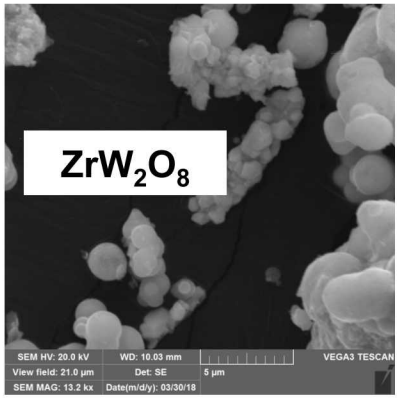
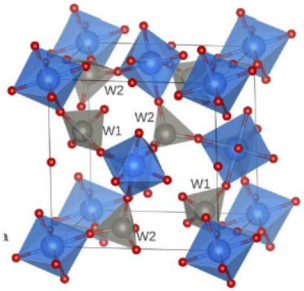
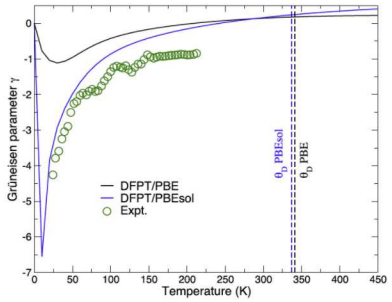
Synthesis
(cubic ZrW_2O_8 and $Zr_2P_2WO_{12}$)

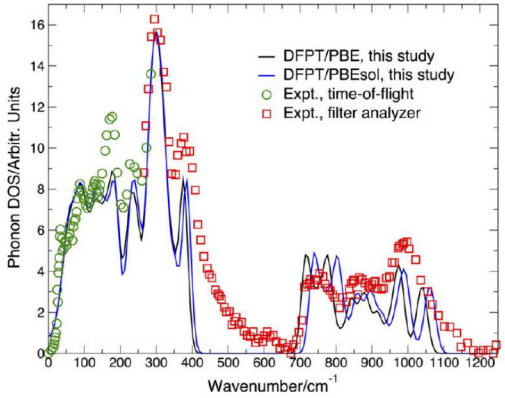


DFT/DFPT calculations
(structure, vibrational, thermodynamics, and thermo-mechanical properties, etc)

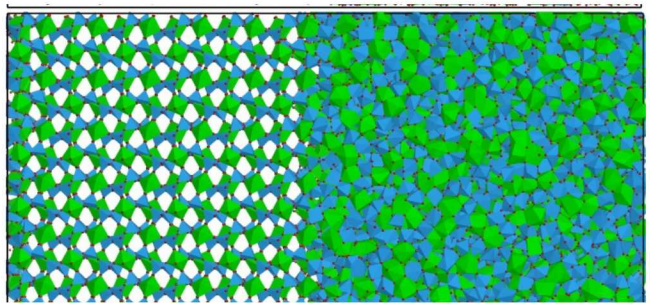




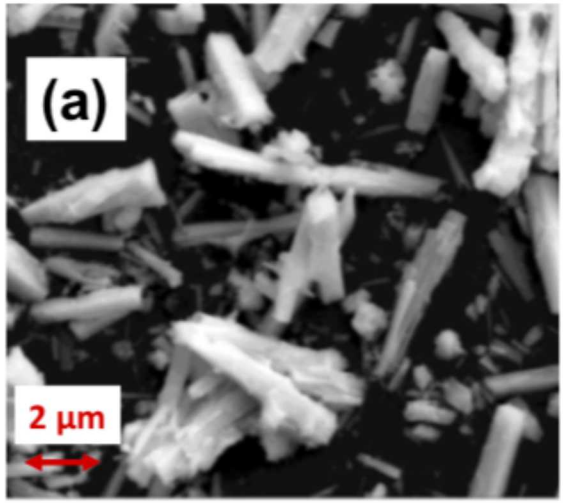
Characterization
(XRD, mid/far-IR, Raman)

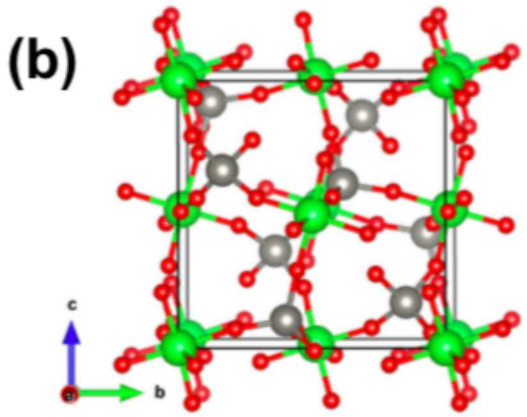


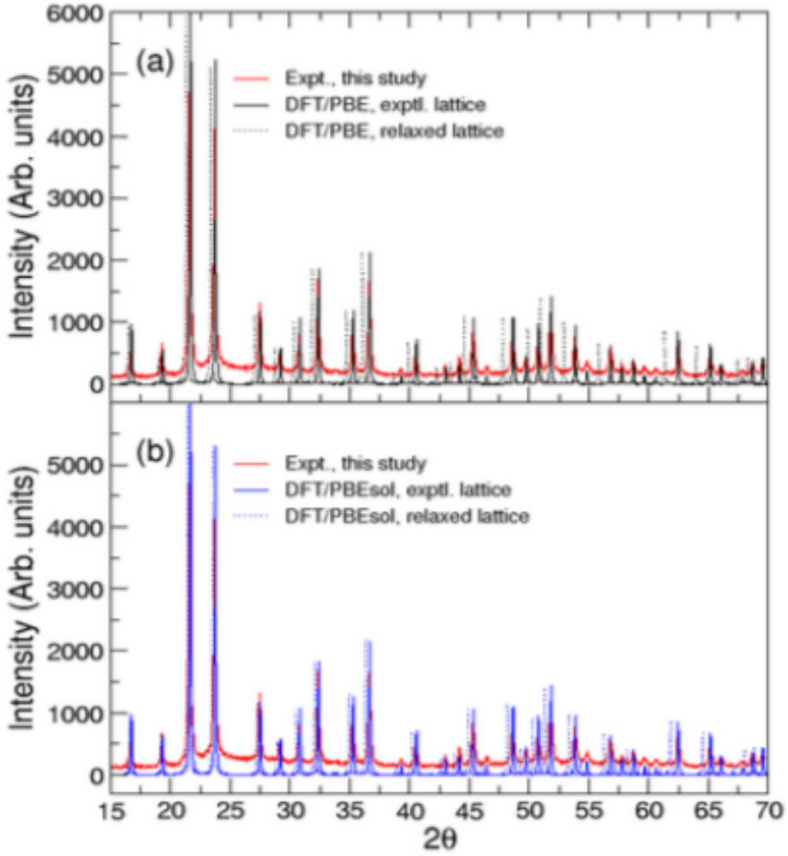
LAMMPS simulations
(MD models for amorphization, crystal/ amorphous material boundary)



Zr Tungstate



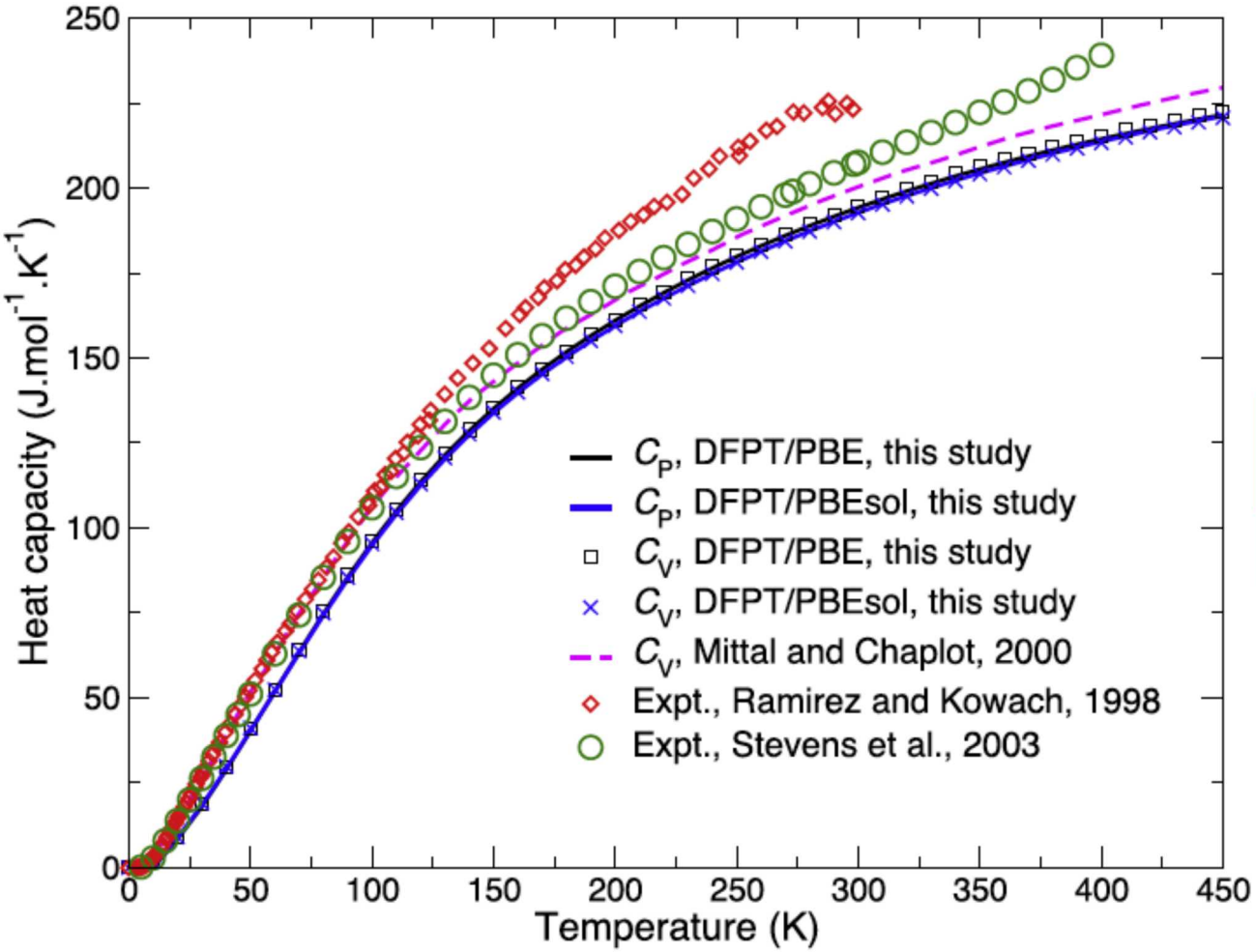




	DFT		Expt.	
	PBE	PEBsol	This work	Evans et al.
a (Å)	9.310	9.241	9.1493	9.1846

α–ZrW_2O_8 (space group $P2_13$; IT No. 198; Z=4) with corner-sharing ZrO_6 octahedral and WO_4 tetrahedral coordination units [Weck et al., Chem. Phys. Lett. 698, 195 (2018)].

Thermal properties of α–ZrW_2O_8



$$C_P(T,P) = -T\frac{\partial^2 G(T,P)}{\partial T^2} = T\frac{\partial V(T,P)}{\partial T}\frac{\partial S(T,V)}{\partial V}\Big|_{V=V(T,P)} + C_V[T,V(T,P)],$$

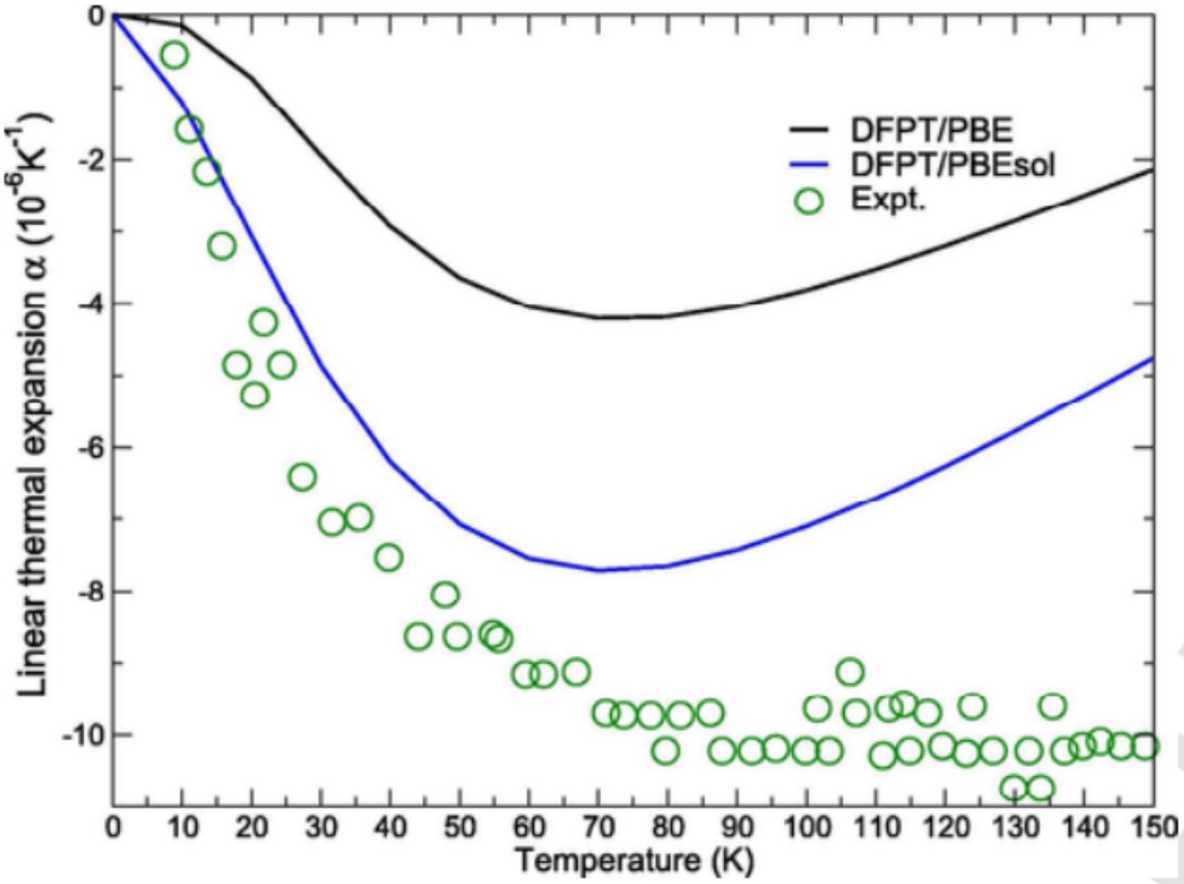
$$C_V = k_B \sum (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega}-1]^2}$$

	C_P^0 (J/mol/K)
DFT	193.8 [1]
Expt	207.01[2]; 223.3 [3]

[1] Weck et al., 2018.
[2] Stevens et al., 2003.
[3] Ramirez and Kowach, 1998.

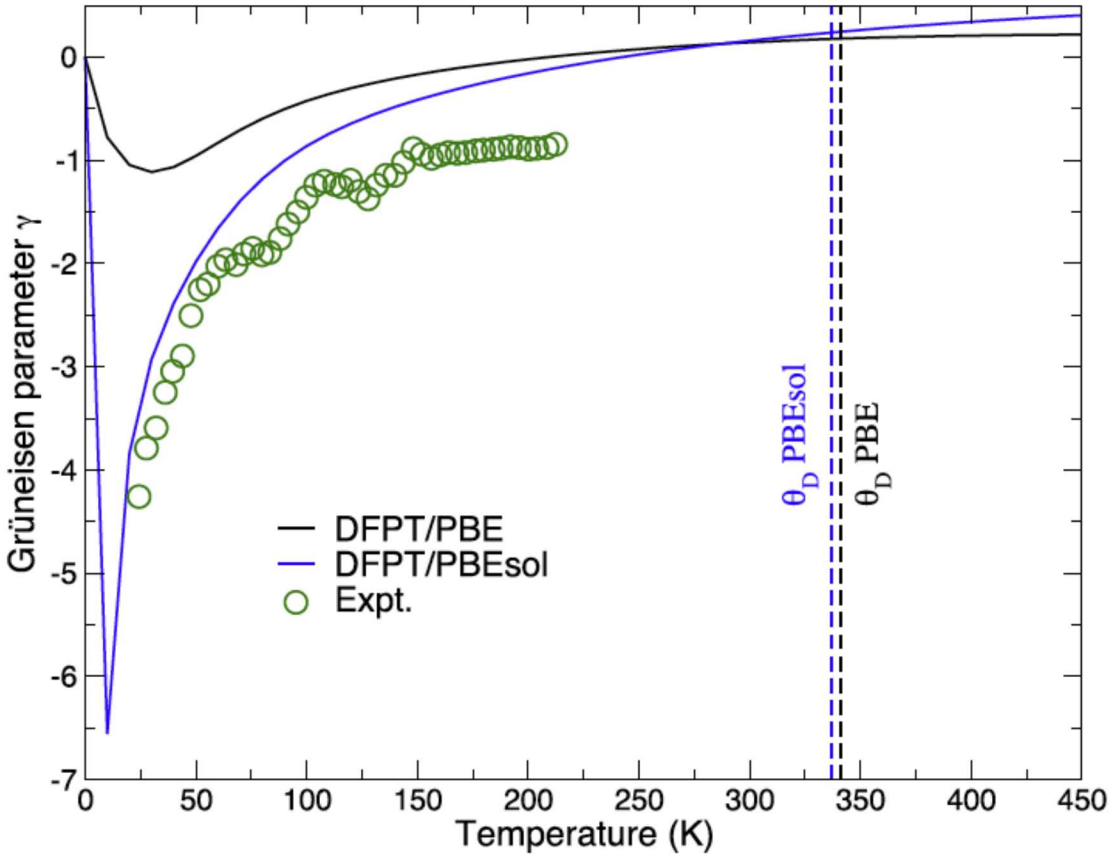
Thermal evolution of the molar isochoric (C_V) and isobaric (C_P) heat capacities of alpha-ZrW_2O_8 calculated at constant atmospheric pressure using DFT at the GGA/PBE and GGA/PBEsol levels within the quasi-harmonic approximation.

Linear coefficient of thermal expansion (CTE) of $\alpha-ZrW_2O_8$



- The linear CTE computed using PBEsol is in very good agreement with the experimental data from the high-resolution neutron diffraction measurements of David et al. (1999) to ~60K
- The PBEsol linear CTE reaches an extremum of at ~70K
- Similar discrepancies were found above ~60K between these experimental data [6] and the finite-displacement B3LYP calculations of Gava et al. (2012)

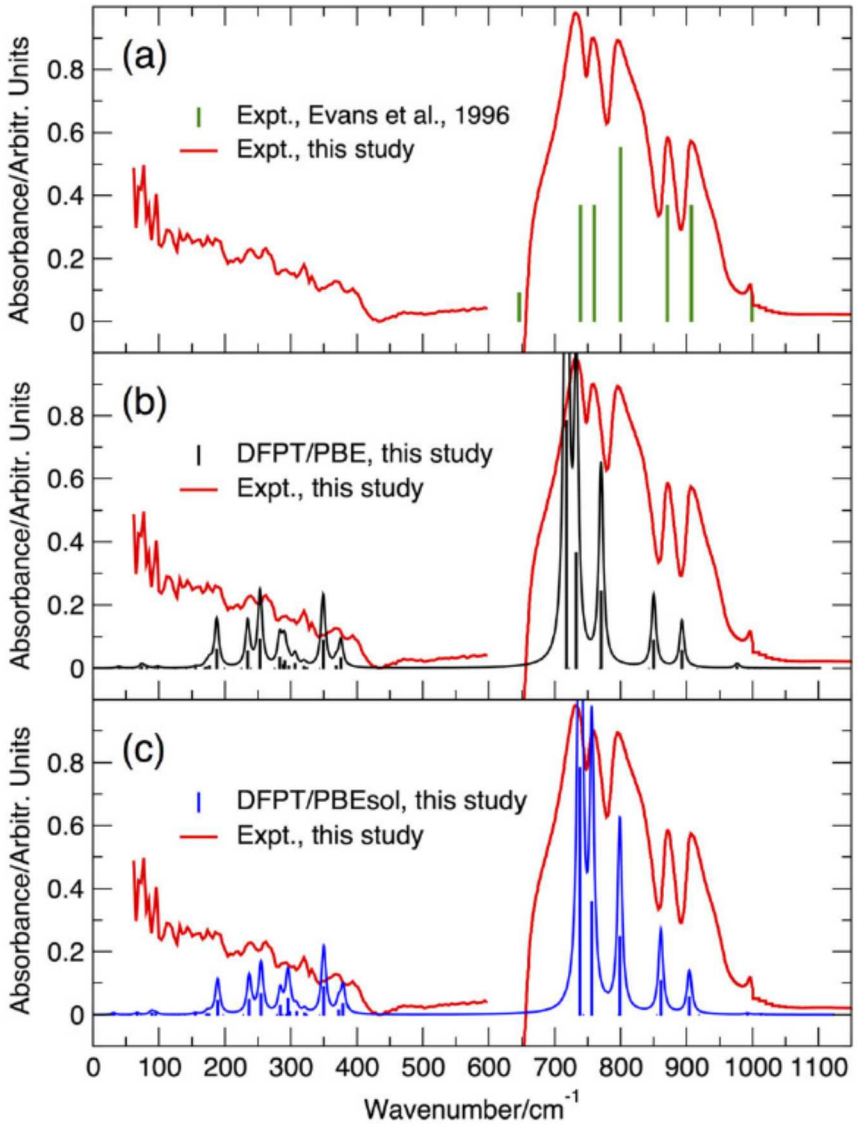
Grüneisen parameter of α–ZrW_2O_8



- PBEsol results are in excellent agreement with the experimental Grüneisen parameter by Ernst et al. (1998) to 60K.
- The main contributions to NTE at low temperature stem from the two lowest-frequency optical phonons, predicted at 36 cm^{-1} (T_{irrep}) and 37 cm^{-1} (E_{irrep}).
- These modes are characterized by variations of intrapolyhedral bond angles O-M-O (M = W, Zr), achieved though combined librational and translational motions of WO_4 units.

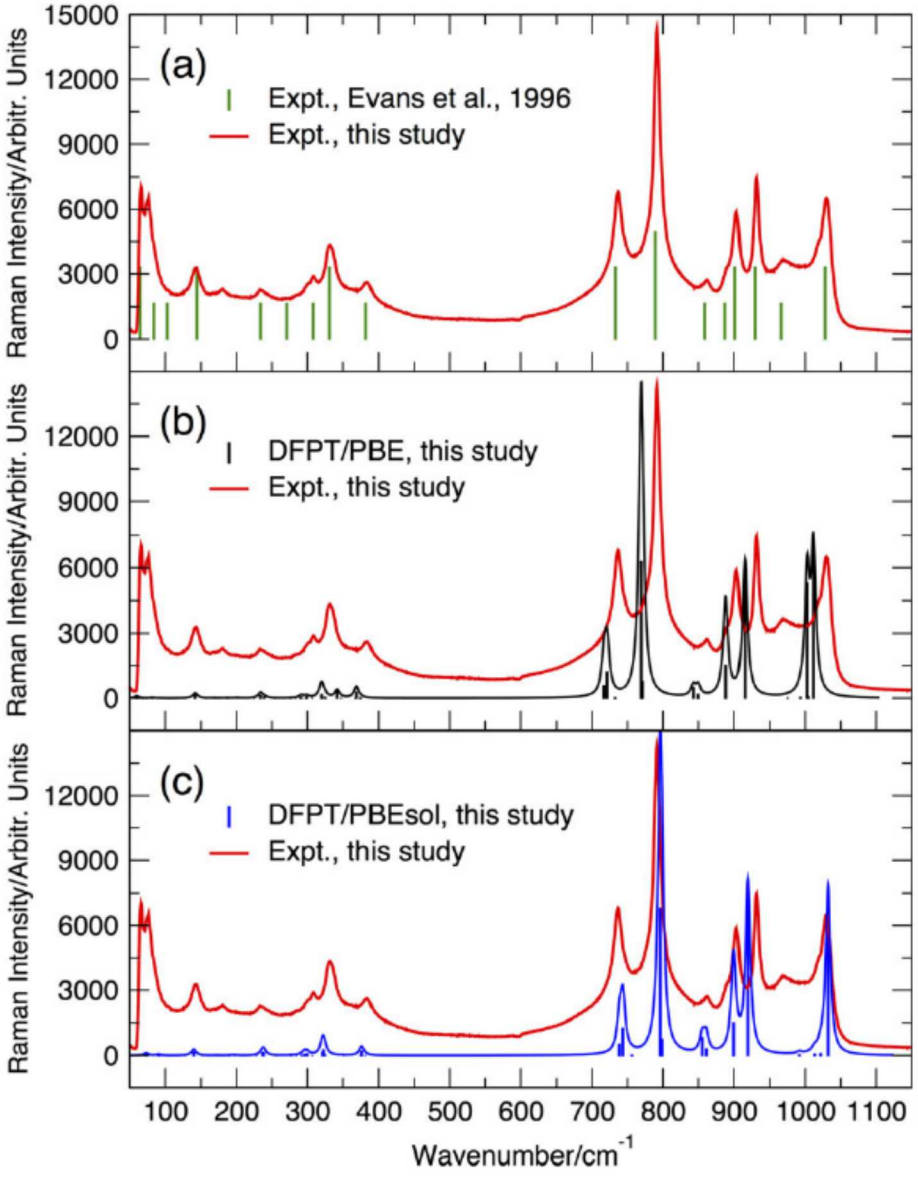
Thermal evolution of the Grüneisen parameter of alpha-ZrW_2O_8 calculated using DFT at the GGA/PBE and GGA/PBEsol levels within the quasi-harmonic approximation.

IR spectrum of α–ZrW_2O_8



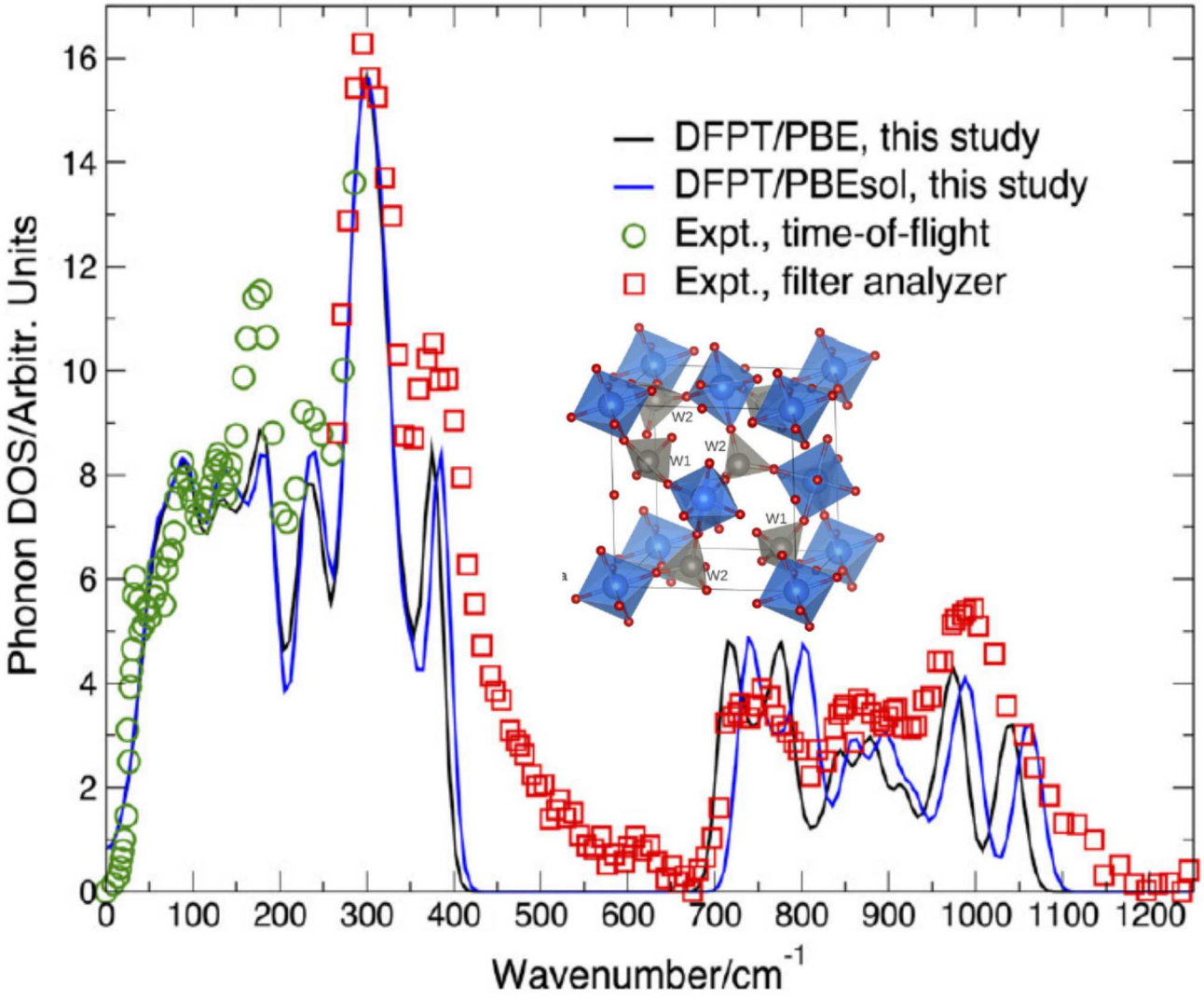
- Fourier transform infrared (FT-IR) spectra of α-ZrW_2O_8 measured in this study at T = 298 K (red line) and observed IR band centers reported by Evans et al. (green lines), along with infrared spectra simulated from DFPT at the GGA/PBE (black) and GGA/PBEsol (blue) levels
- The IR spectrum simulated using PBEsol is in close agreement with experiments
- The IR-active wavenumber observed by Evans et al. at 646 cm^{-1} along with several weak lines in the range 600–400 cm^{-1} were not predicted by DFPT calculations, nor observed in the present experiments

Raman spectrum of α–ZrW_2O_8



- Raman spectrum of α-ZrW_2O_8 measured in this study at T = 298 K (red) and observed and calculated Raman band centers reported by Evans et al. (green), along with Raman spectra simulated from DFPT-PBE (black) and DFPT-PBEsol (blue) levels
- No 855-628 cm^{-1} peaks appear in the α-ZrW_2O_8 Raman bands predicted with DFPT or measured in this study or by Evans et al
- No stable ZrO_2 or WO_3 present in the sample
- Similar to PDOS and IR DFPT calculations, no Raman active modes are predicted to occur in the ranges 381–739 cm^{-1} and 374–717 cm^{-1} with PBEsol and PBE, respectively

Phonon density of states (PDOS) of α–ZrW_2O_8



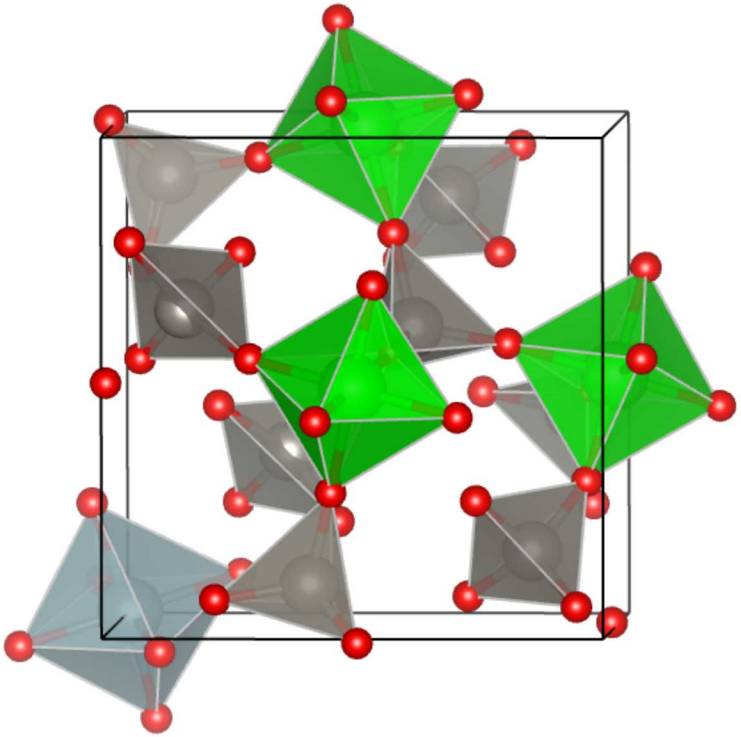
Phonon density-of-states (PDOS) spectra of α-ZrW_2O_8 simulated at T = 0 K using density functional perturbation theory (DFPT) at the GGA/PBE (black line) and GGA/PBEsol (blue line) levels. The generalized PDOS spectrum from inelastic neutron scattering data collected at T = 300 K using time-of-flight (green circles) and filter-analyzer (red squares) spectroscopy is shown for comparison

Conclusion

- DFPT calculations were conducted at the GGA/PBE and GGA/PBEsol levels of theory to systematically investigate the crystal structure, phonon, IR and Raman spectra, and vibrational properties of α-ZrW_2O_8
- DFPT calculations were able to correctly reproduce the NTE behavior, elastic/mechanical properties, and IR/Raman spectra of ZrW_2O_8
- The calculated thermodynamic/thermo-mechanical properties were validated with measured data
- Calculations for $Zr_2P_2WO_{12}$ are being finalized and also appear to reproduce available experimental data

Current/future research

1. U/Pu/Tc inclusion in α−ZrW_2O_8



2. DFT Modeling of $Zr_2P_2WO_{12}$