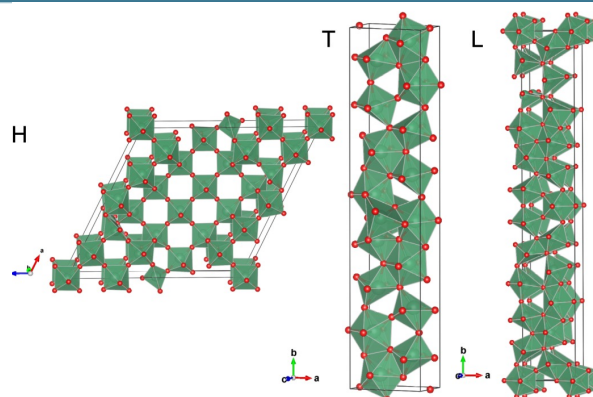




# Pressure-Induced Transformation of $\text{Nb}_2\text{O}_5$ Under Shock Compression From First Principles



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APS Topical Group on Shock Compression of Condensed Matter (SCCM23)

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Chicago, IL, Friday, June 23, 2023, 12:15 PM–12:30 PM

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- **Pressure-induced amorphization (PIA)** has emerged as a powerful way for **synthesis of recoverable amorphous materials with novel properties**
- PIA-synthesized amorphous phases may retain some properties related to crystalline parent phase → **PIA-synthesized phases may be different from traditional amorphous phases**
- Early PIA observations were in ice-H<sub>2</sub>O, **tetrahedrally-coordinated materials** (e.g., Si and SiO<sub>2</sub>), and **octahedrally-coordinated materials** (e.g., TiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>)
- PIA was also observed in some **M<sub>2</sub>O<sub>5</sub> materials with complicated coordination polyhedra** and other complex materials (e.g., perovskite, (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> olivine, ZrW<sub>2</sub>O<sub>8</sub> tungstate,...)
- **Structural relations and transformation mechanisms** between the crystalline parent phase and PIA-synthesized amorphous phases **often remain unclear**

# Motivation to Study Phase Transitions and PIA in Nb<sub>2</sub>O<sub>5</sub>



- **Nb<sub>2</sub>O<sub>5</sub> features interesting properties:**
  - High dielectric constant
  - High refractive index
  - Interesting photoelectric/photocatalytic properties
  - High chemical stability and corrosion resistance
- **Nb<sub>2</sub>O<sub>5</sub> used in numerous applications:**
  - Special optical glasses (e.g., electrochromic glass)
  - Chemical fiber panels
  - Monolithic capacitors
  - Piezoelectric ceramic elements
  - Gas sensors
  - Solar cells
  - Photocatalysts

# Nb<sub>2</sub>O<sub>5</sub> Polymorphs and PIA: Observation and Knowledge Gaps



## ■ Many commonly observed Nb<sub>2</sub>O<sub>5</sub> polymorphs:

- Monoclinic H-phase (room temperature phase; *P2/m*; NbO<sub>6</sub> coordination)
- Orthorhombic T-phase (*Pbam*; NbO<sub>6</sub> and NbO<sub>7</sub> coordination)
- Monoclinic B-phase (*C2/c*; NbO<sub>6</sub> coordination)
- Monoclinic N- and R-phases (*C2/m*; NbO<sub>6</sub> coordination)
- Tetragonal M-phase (*I4/mmm*; NbO<sub>6</sub> coordination)
- Tetragonal P-phase (*I4<sub>1</sub>22*; NbO<sub>6</sub> coordination)
- Pseudo-hexagonal/monoclinic TT-phase (*Pmba*; NbO<sub>6</sub> and NbO<sub>7</sub> coordination)

## ■ Phase transitions and PIA in Nb<sub>2</sub>O<sub>5</sub>:

- **H-Nb<sub>2</sub>O<sub>5</sub> → T-Nb<sub>2</sub>O<sub>5</sub> at ~14-20 GPa under shock**, with **T decomposing into NbO<sub>2</sub> at ~40 GPa** (Kikuchi et al., 1985, 1986)
- **PIA observed in T-Nb<sub>2</sub>O<sub>5</sub> at ~19.2 GPa at 300 K** accompanied by Nb reduction (Serghiou et al., 1992)
- XPS and XAS experiments showed **no pressure-induced Nb reduction in T-Nb<sub>2</sub>O<sub>5</sub> near PIA pressure** (Tse et al., 1994)
- In situ synchrotron XRD shows **H-Nb<sub>2</sub>O<sub>5</sub> → L-Nb<sub>2</sub>O<sub>5</sub> at ~9 GPa (orthorhombic L-Ta<sub>2</sub>O<sub>5</sub>-type Nb<sub>2</sub>O<sub>5</sub> phase) under hydrostatic pressure**, followed by **PIA-synthesized phase above 21.4 GPa** (Guan et al., 2019)
- **No clear understanding of structural relation and transformation mechanisms between the crystalline H-Nb<sub>2</sub>O<sub>5</sub> parent phase and PIA-synthesized amorphous phase**

Kikuchi et al., Japan J. Appl. Phys., 24, 1600 (1985); J. Solid State Chem., 63, 386 (1986)

Serghiou et al., PRL, 68, 3311 (1992)

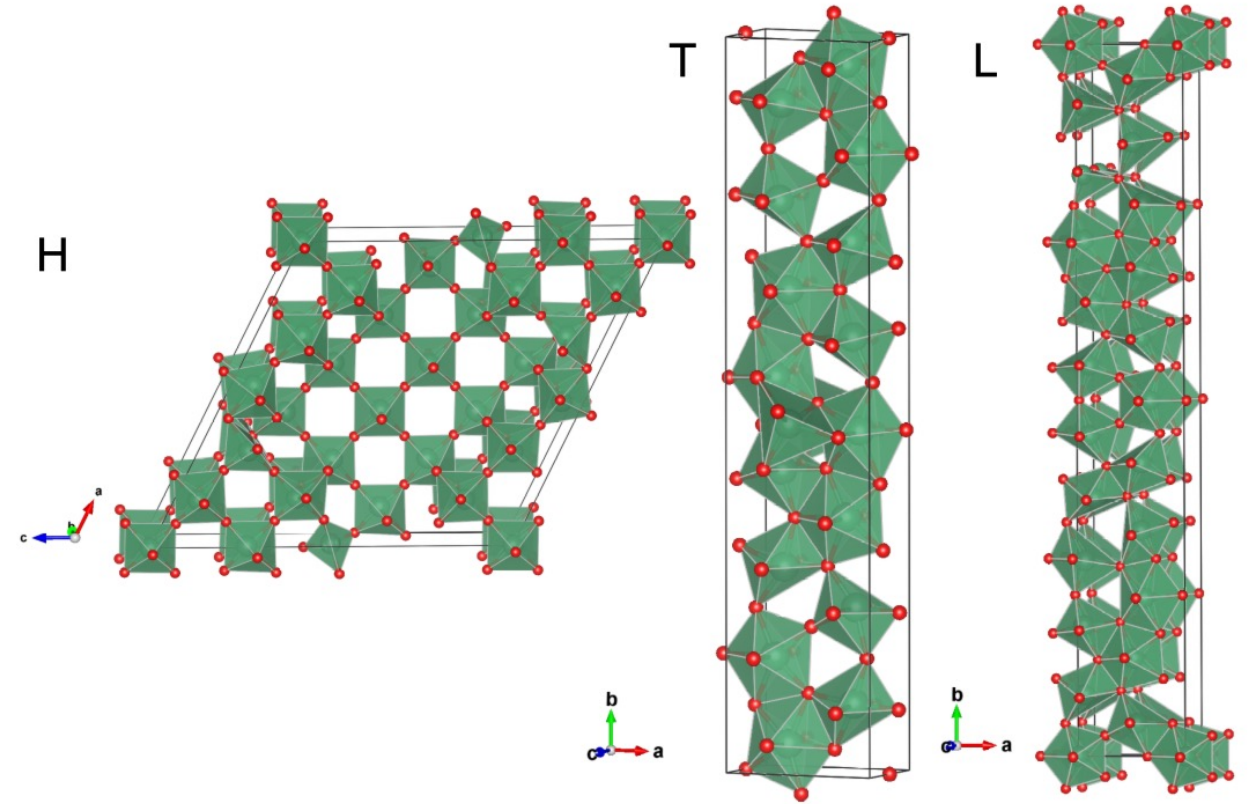
Tse et al., PRB, 49, 9180 (1994)

Guan et al., J. Phys.: Cond. Matter, 31, 105401 (2019)

# Goals of This Computational Study



- **Using ab initio molecular dynamics (AIMD) simulations to:**
  - Extend our previous simulations on shock compression of Nb, NbO and NbO<sub>2</sub> to Nb<sub>2</sub>O<sub>5</sub> (Weck et al., 2019, 2020)
  - Build tabular equations of states (EOS) of Nb<sub>2</sub>O<sub>5</sub> polymorphs for use in the development of multiphase SESAME-type EOS
  - Provide insights into the phase transformations and PIA in Nb<sub>2</sub>O<sub>5</sub>
  
- **Nb<sub>2</sub>O<sub>5</sub> polymorphs considered in this study:**
  - Monoclinic **H phase** (*P2/m*, IT #10)
  - Orthorhombic **T phase** (*Pbam*, IT #55)
  - Orthorhombic **L phase** (L-Ta<sub>2</sub>O<sub>5</sub>-type phase, *Pmm2*, IT #25).



Ball-and-stick representation of periodic crystal cells of H-, T-, and L-phases of Nb<sub>2</sub>O<sub>5</sub>. O: red; Nb: green

Weck et al., J. Appl. Physics, 125, 245905 (2019)

Weck et al., AIP Conference Proceedings 2272, 070053 (2020)



## ■ AIMD simulations:

- **Vienna Ab initio Simulation Package** (VASP), with Mermin's generalization of the Kohn-Sham equations to finite temperature
- **Generalized Gradient Approximation** (GGA), with the **Perdew-Burke-Ernzerhof** (PBE) XC functional
- Projector Augmented Wave (PAW) pseudopotentials
- **Canonical (NVT ensemble)** simulations to calculate isotherms in the ranges 300-2500 K
- 0.7 fs time step for ion motion; energy and pressure averaging over several picoseconds
- Plane-wave cutoff energy set to 700 eV

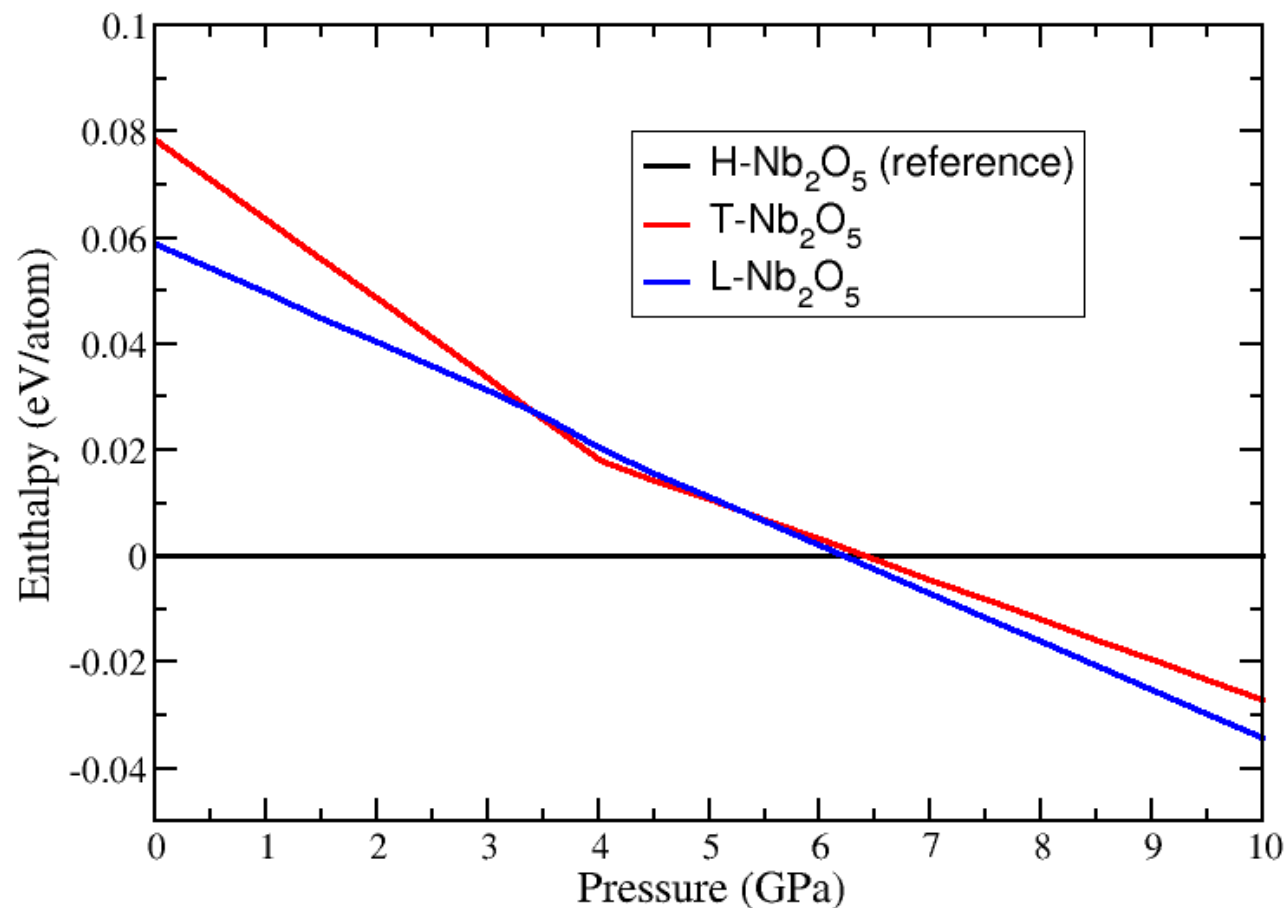
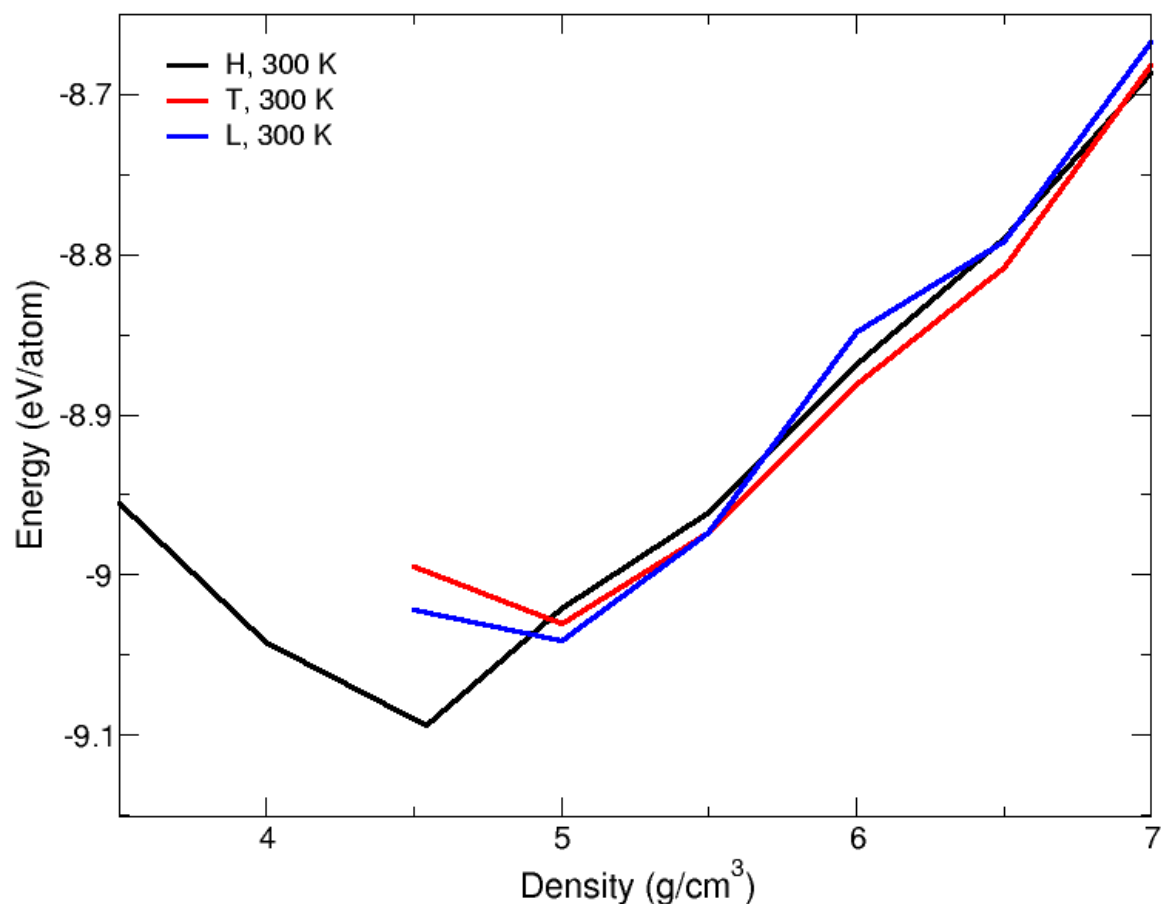
## ■ Shock Hugoniot:

- **Principal Hugoniot calculated from AIMD-generated tabular EOS** for polymorphs, using a reference density of 4.54 g/cm<sup>3</sup> (TMD) at 300 K for H-Nb<sub>2</sub>O<sub>5</sub>
- Hugoniot curve consists of (P; V; T) points satisfying the **Hugoniot relation**:

$$E - E_0 + (1/2)(P + P_0)(V - V_0) = 0$$

where  $E$ : specific internal energy;  $P$ : pressure;  $V$ : volume =  $1/\rho$ ; and  $E_0, P_0, V_0$ : reference energy, pressure and volume at 300 K

# AIMD predictions @ 300 K: H $\rightarrow$ L vs. H $\rightarrow$ T

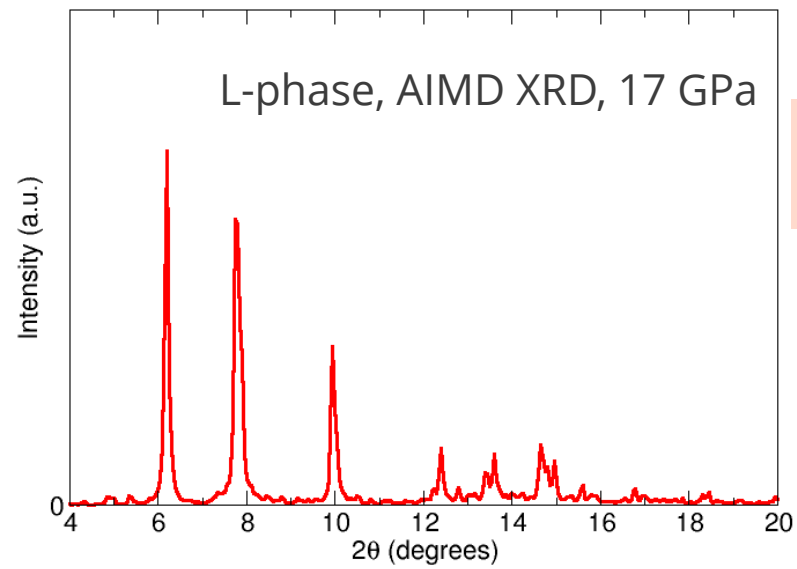
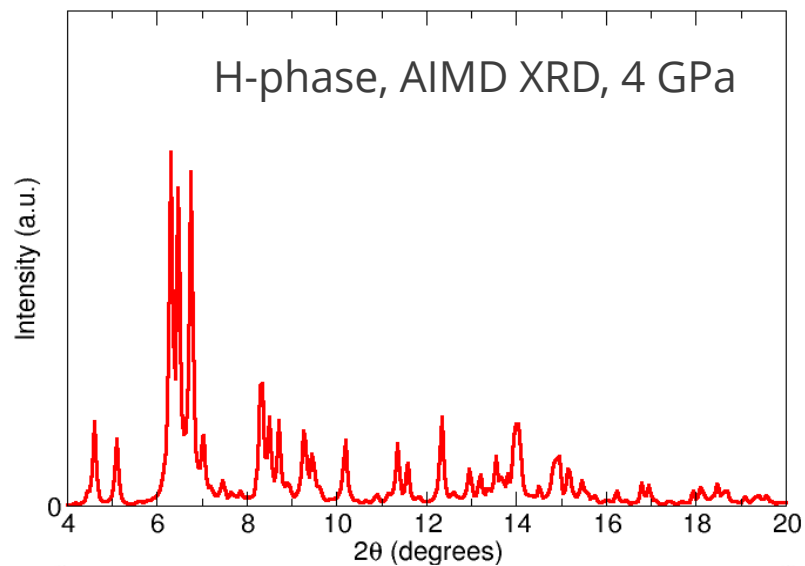
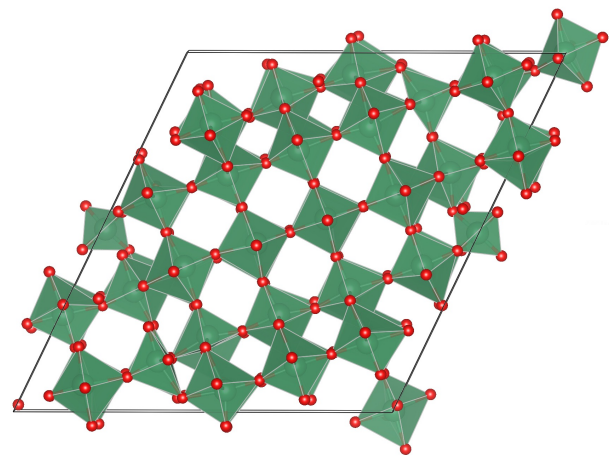


- H $\rightarrow$ L transformation more favorable than H $\rightarrow$ T under hydrostatic conditions at 300K, with small energy differences between L and T phases predicted from AIMD simulations
- Enthalpy derived from AIMD simulations @ 300 K shows H $\rightarrow$ L at 6.2 GPa and H $\rightarrow$ T at 6.4 GPa
- Excellent agreement with XRD: H-phase indexed below 4.7 GPa; new peaks appear at ~5.9 GPa; no H peaks at 9.9 GPa (Guan et al., 2019).

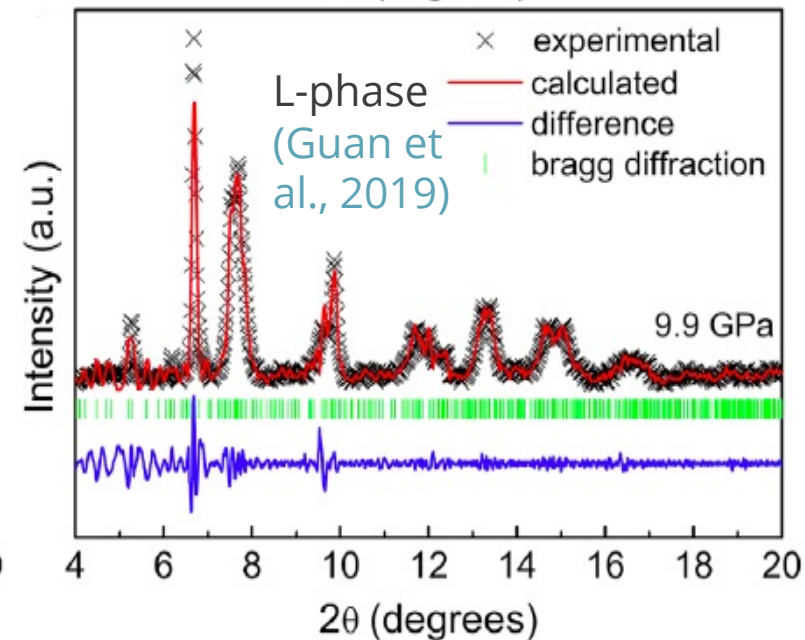
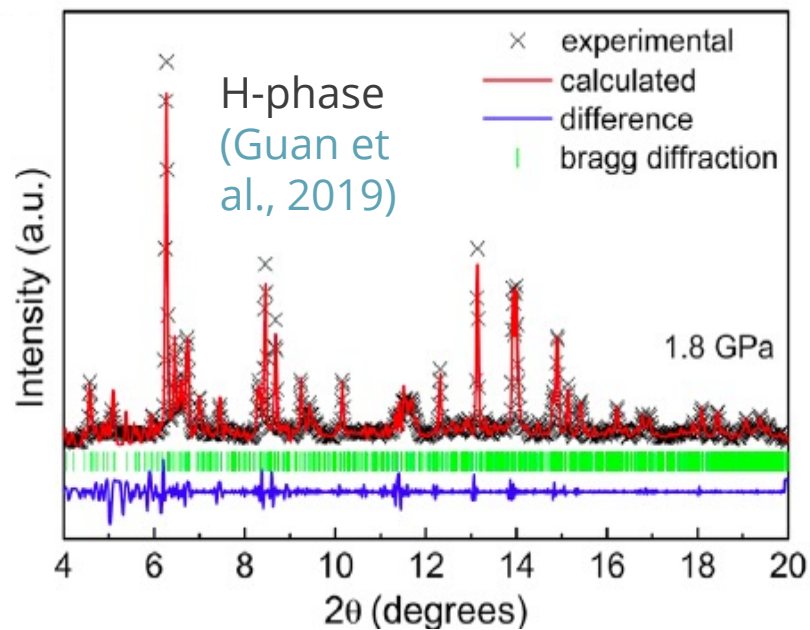
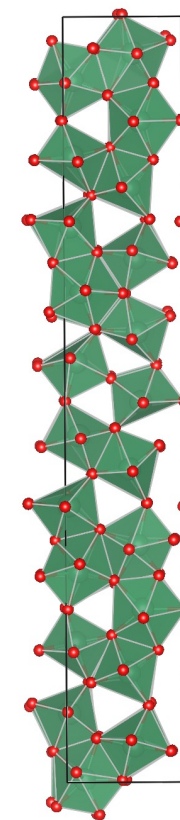
# XRD expt. and AIMD predictions @ 300 K



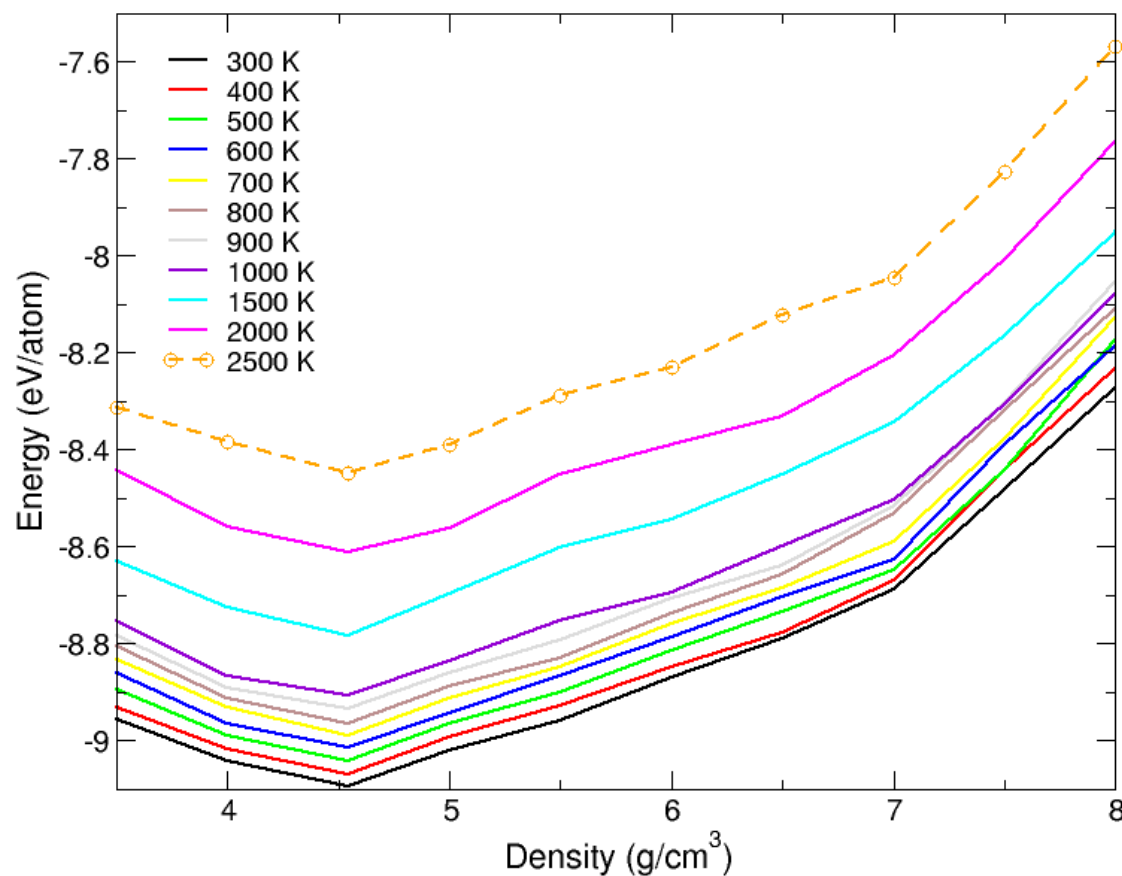
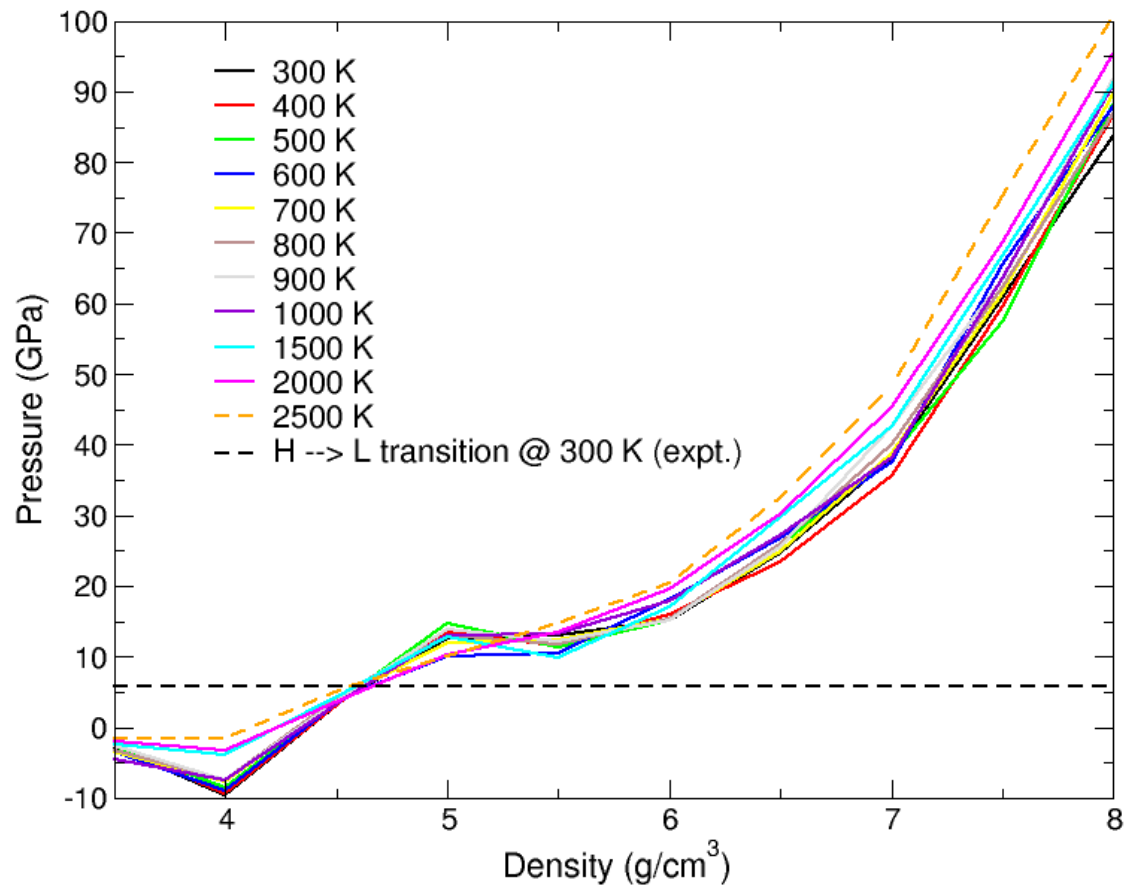
AIMD-relaxed monoclinic  
H-Nb<sub>2</sub>O<sub>5</sub> at 300 K



AIMD-relaxed  
orthorhombic L-  
Nb<sub>2</sub>O<sub>5</sub> at 300 K

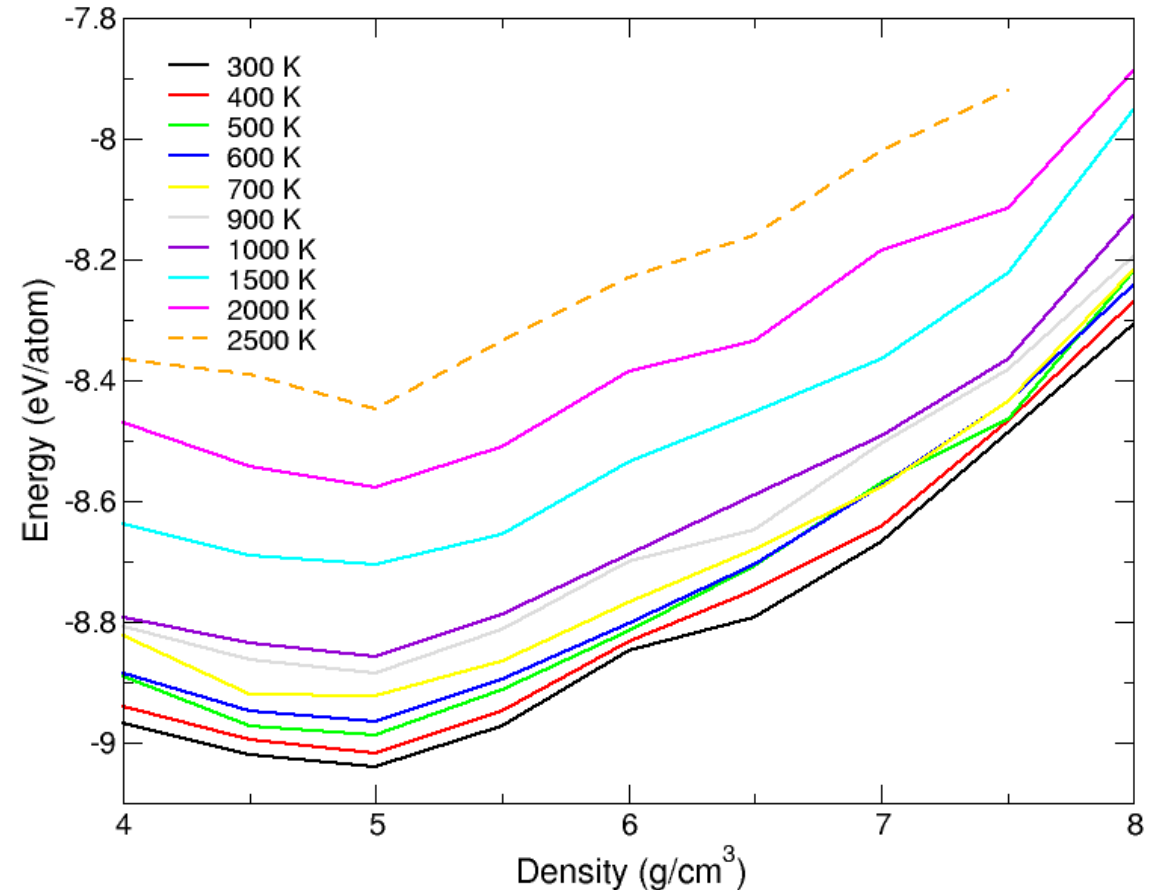
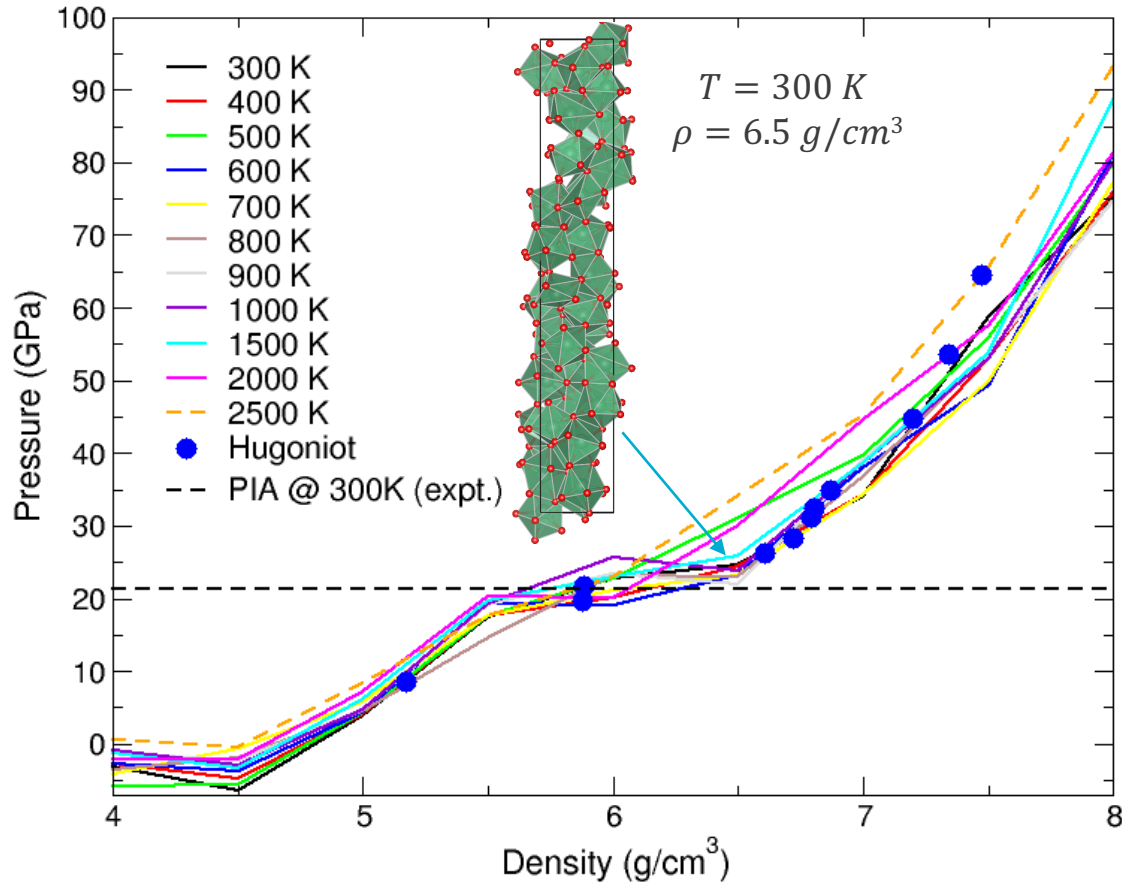


# AIMD Tabular EOS for H-Nb<sub>2</sub>O<sub>5</sub>



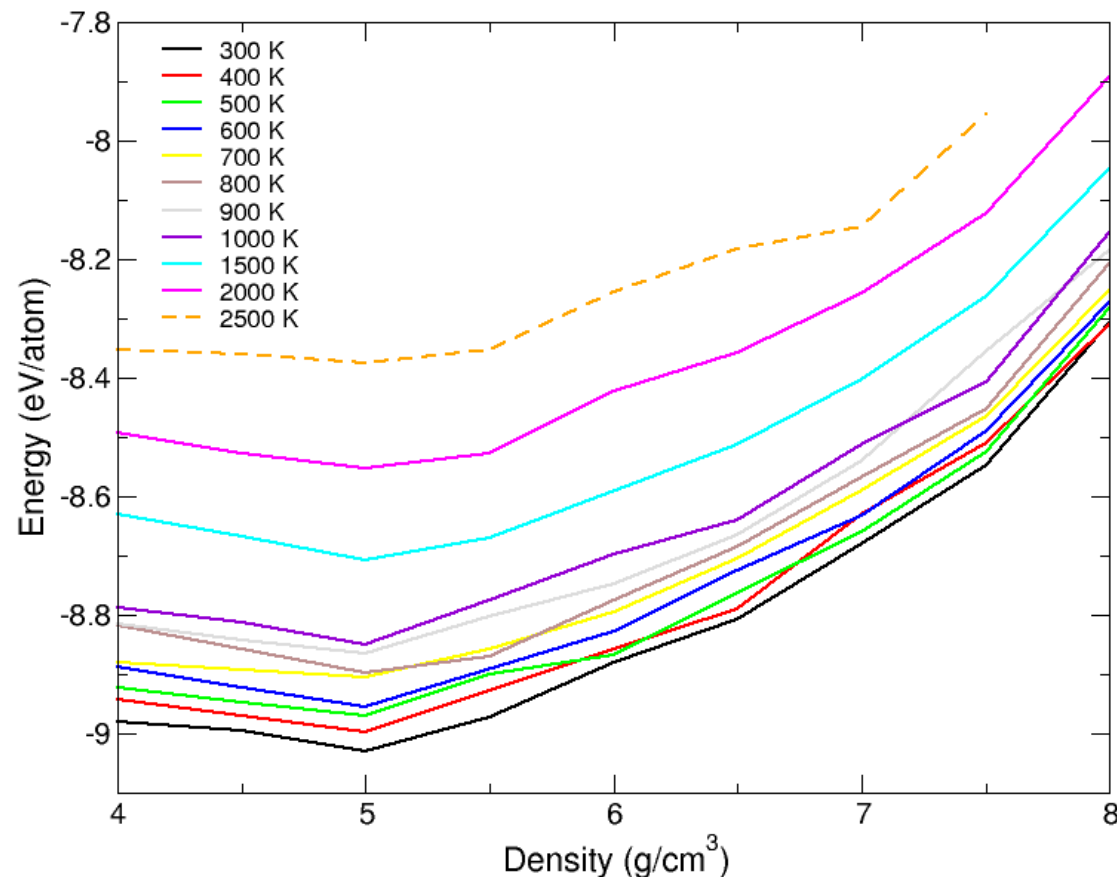
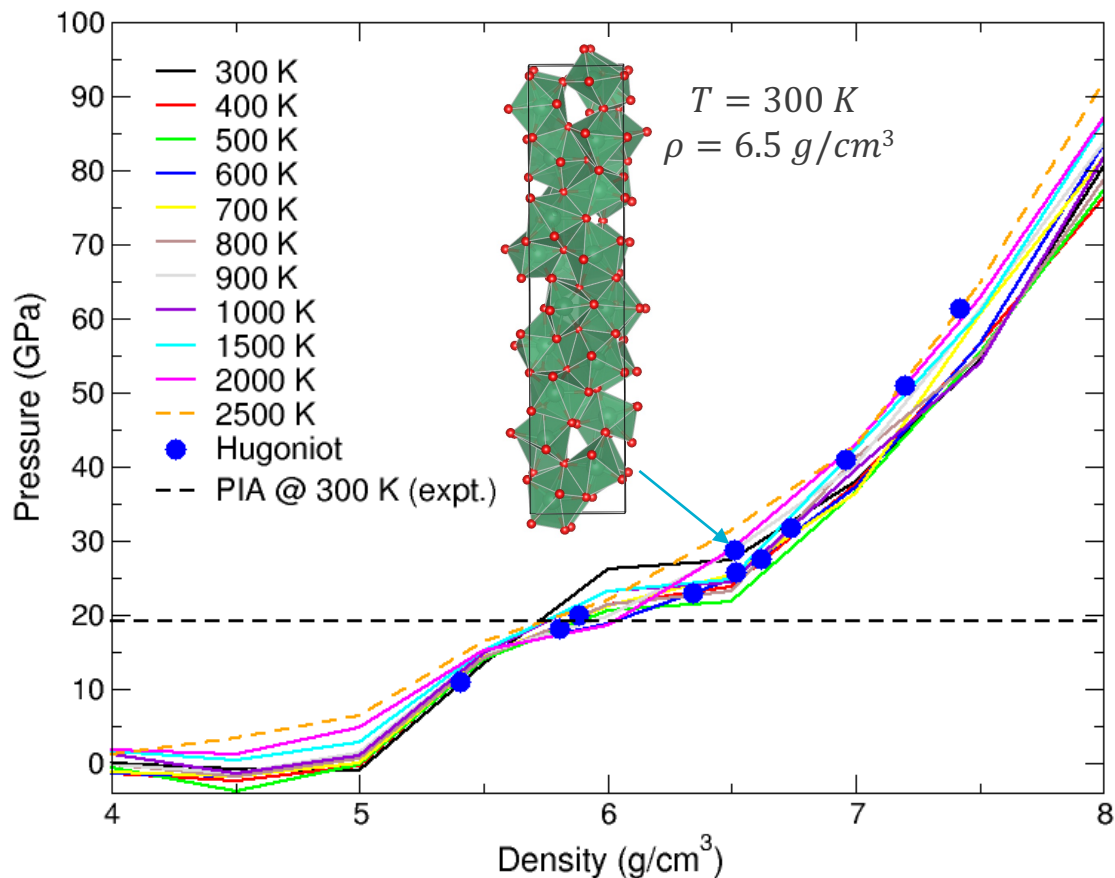
- Only relatively small pressure differences as a function of temperature predicted from AIMD simulations in the 300-2,500 K range in the vicinity of H→L transition [ $\sim 5.9$  GPa (Guan et al., 2019)]

# AIMD Tabular EOS for L-Nb<sub>2</sub>O<sub>5</sub> and Hugoniot



- AIMD simulations predict PIA of L-phase between ~18 and ~25 GPa, for densities in the range 5.5-6.5  $\text{g/cm}^3$
- Pressure for PIA is nearly temperature independent in 300-2500 K range
- Excellent agreement with XRD experiments: PIA-phase synthesized from L-phase observed above 21.4 GPa at 300 K (Guan et al., 2019)

# AIMD Tabular EOS for T-Nb<sub>2</sub>O<sub>5</sub> and Hugoniot



- AIMD simulations predict PIA of T-phase between ~16 and ~26 GPa**, for densities in the range ~5.5-6.5  $\text{g/cm}^3$ , very similar to PIA from L-phase
- Similar to PIA of L-phase, **PIA of T-phase is nearly temperature independent**
- Excellent agreement with XRD experiments: PIA-phase synthesized from T-phase observed above 19.2 GPa at 300 K** (Serghiou et al., 1992)

# Conclusion



- Tabular EOS of H-, L- and T-Nb<sub>2</sub>O<sub>5</sub> polymorphs were calculated from AIMD simulations for future use in the development of multiphase SESAME-type EOS
- AIMD simulations predict that **H→L transformation is more favorable than H→T under hydrostatic conditions at 300K**, with small energy differences between L and T phases
- Enthalpy derived from AIMD simulations @ 300 K shows **H→L at 6.2 GPa** and **H→T at 6.4 GPa**, in excellent agreement with XRD data showing **new peaks for orthorhombic phase appear at ~5.9 GPa**
- Small pressure differences as a function of temperature predicted from AIMD simulations in the 300-2,500 K range in the vicinity of H→L transition
- **AIMD simulations predict nearly temperature-independent PIA of L-phase between ~18 and ~25 GPa**, in excellent agreement with XRD data showing **PIA above 21.4 GPa**
- Principal Hugoniot of Nb<sub>2</sub>O<sub>5</sub> was predicted from AIMD in the range 10-60 GPa

## OUTLOOK

- AIMD simulations for additional Nb<sub>2</sub>O<sub>5</sub> polymorphs
- Phonon quasi-harmonic approximation (QHA) calculations to predict thermo-mechanical properties of Nb<sub>2</sub>O<sub>5</sub> polymorphs