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Computational Modeling and Simulation (M&S) of Technetium Containing Materials

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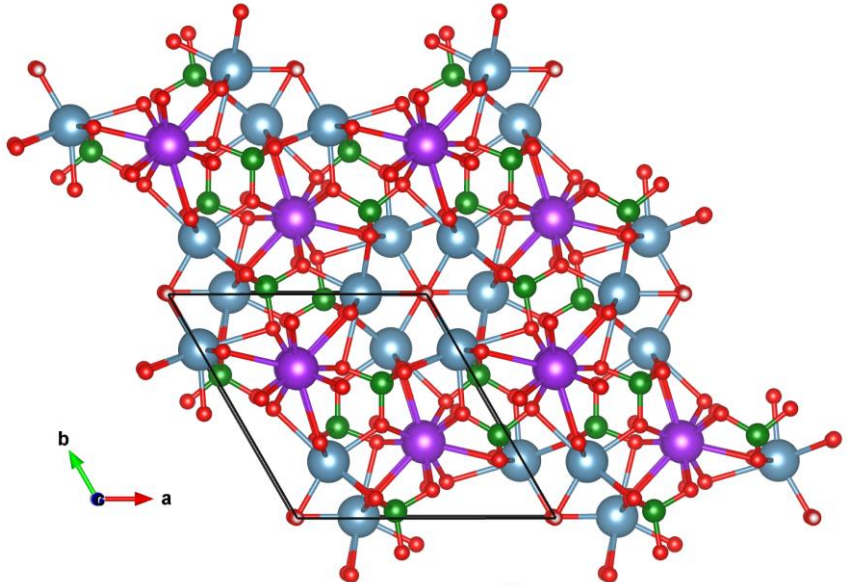
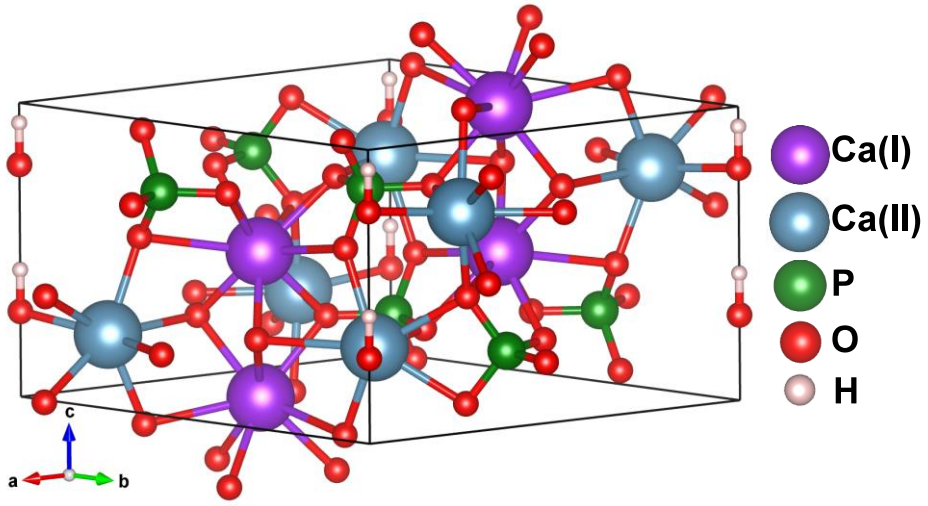
I – Development of Tc Getters for Hanford

Ca-Apatite, $Ca_{10}(PO_4)_6(X)_2$ (X=OH, Cl, F)





Step 1: **Substitution of Sn^{2+} for Ca^{2+} in Ca-apatite**
Ca(I) and/or Ca(II) sites available

Step 2: **Reduction of TcO_4^- with Sn^{2+} in the presence of Sn(II)/Ca-apatite**

Step 3: **Immobilization of Tc with Sn(II)-apatite**
Role of Ca(I)/(II) sites or tetrahedral P sites?
Mechanisms of Tc immobilization?

Objective: Understand the fundamentals of Tc(VII) reduction and association with Sn(II)Apatite

→ Theory: DFT calculations are underway (collaboration Kim@UNLV/Weck@Sandia)

→ Combined theory/expt. effort at SNL [Weck(theory)/Moore(expt.); two patents pending for Moore et al.]

→ **SNL needs some help from EMSL@PNNL with the materials characterization!**

II – Thermodynamics of Tc Compounds

Structure optimization with DFT

- Crystal Structures
  - *Ionic positions*
  - *Lattice Parameters*
- Molar Volumes

Phonon calculations with DF-PT

- Forces on atoms
- Phonon frequencies

Thermodynamic Properties

- Helmholtz free energy, C_V, entropy, enthalpy
- Gibbs free energy, C_P

- **Tc Waste Forms Degradation Models**
- **Thermal Stability of Tc Materials in Geochemical Models**

→ Computational approach successfully applied to predict the thermodynamics of TcX_2 (X = S, Se, Te) compounds (Weck, Kim, Czerwinski (2013), *Dalton Trans.* **42**, 15288).

→ **Objective: apply this approach systematically to other Tc materials used in waste form degradation and geochemical models.**