Atomistic Simulations of Radiation Effects in Ceramics for Nuclear Waste Disposal

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Supported by Nuclear Energy Advanced Modeling and Simulation

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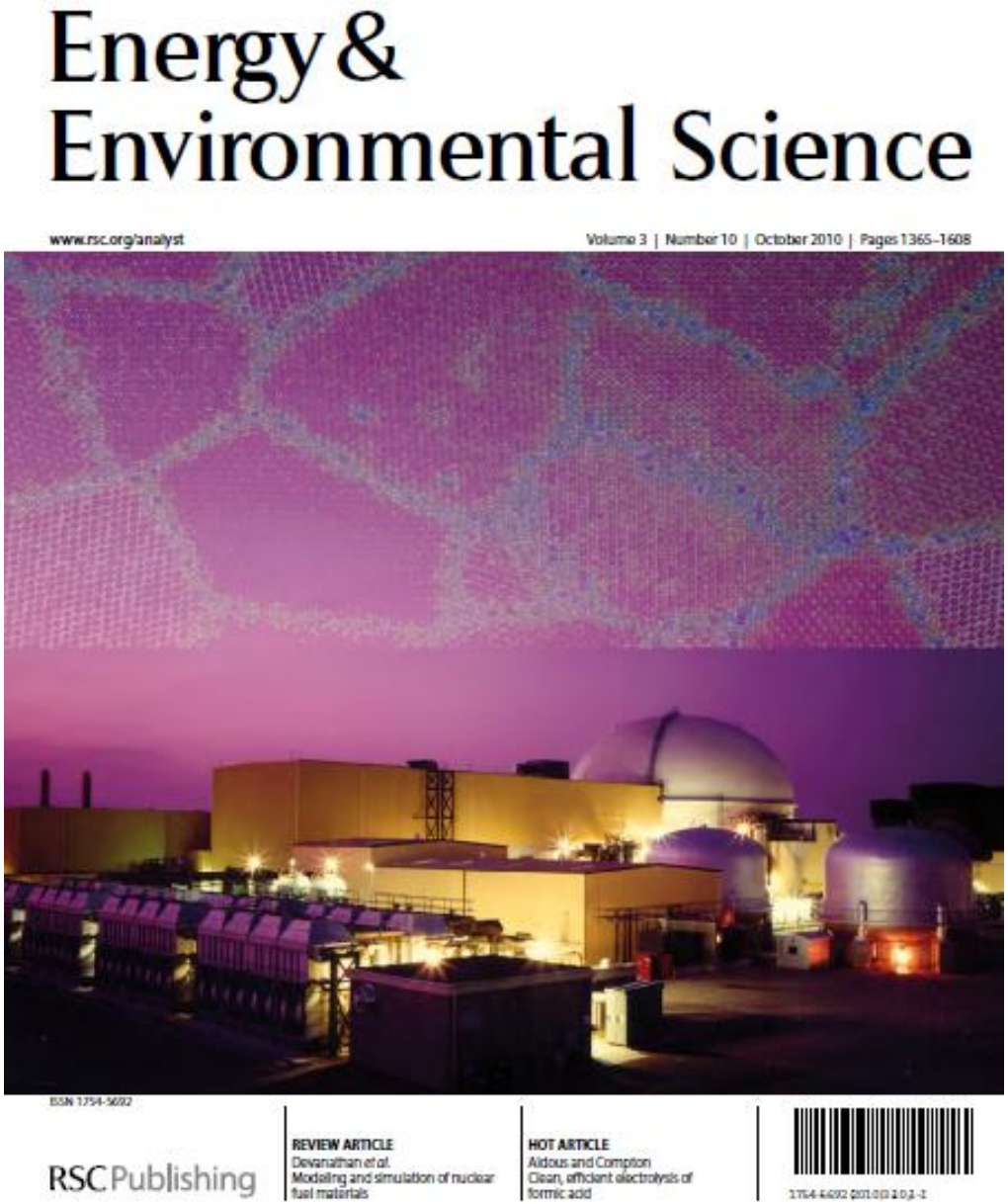
Breaking News



NEAMS-funded review
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Impact factor: 8.5

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Aim and Outline

- Aim: Use fundamental methods & models to understand waste form performance

- Organization of the talk

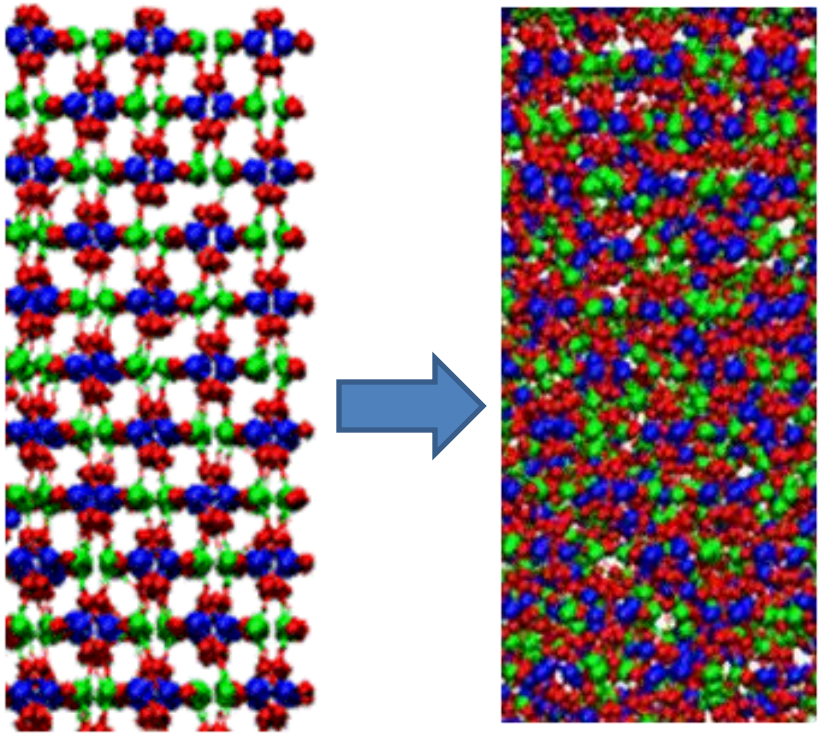
1. Introduction
2. Modeling strategy
3. Potential development
4. Validation
5. Conclusions

- Materials: YPO_4 and $ZrSiO_4$

- Co-workers: Dongsheng Li, Yulan Li, Shenyang Hu

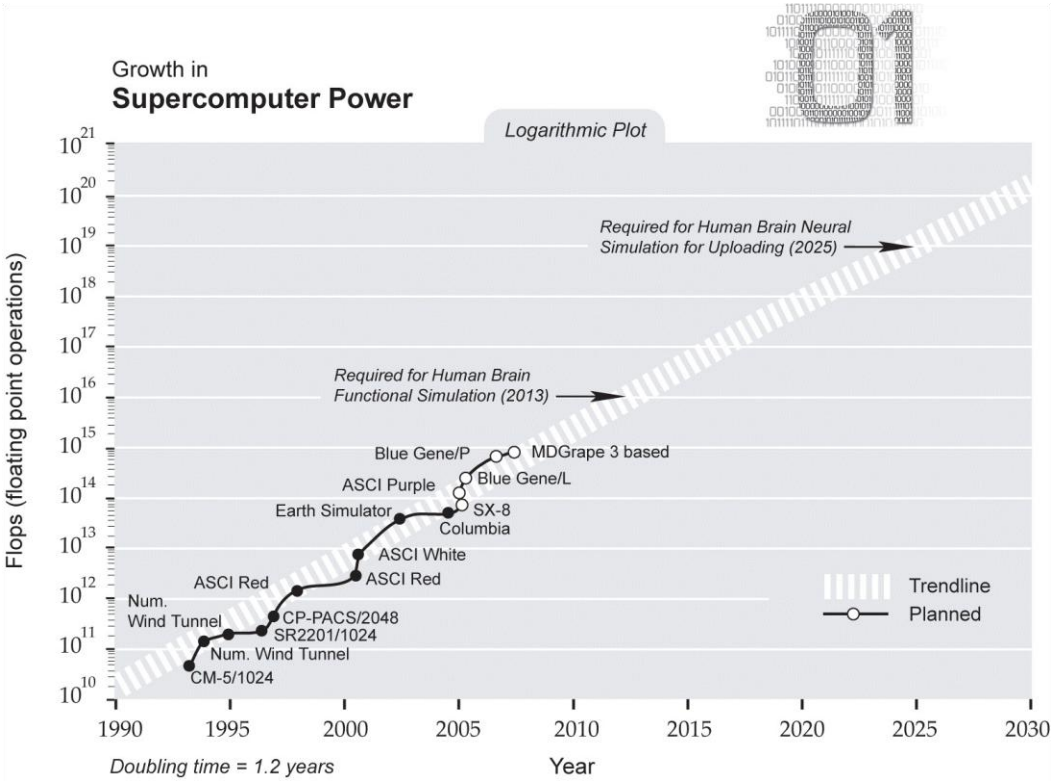
- Funding: Nuclear Energy Advanced Modeling and Simulation

Radiation Effects in Waste Forms



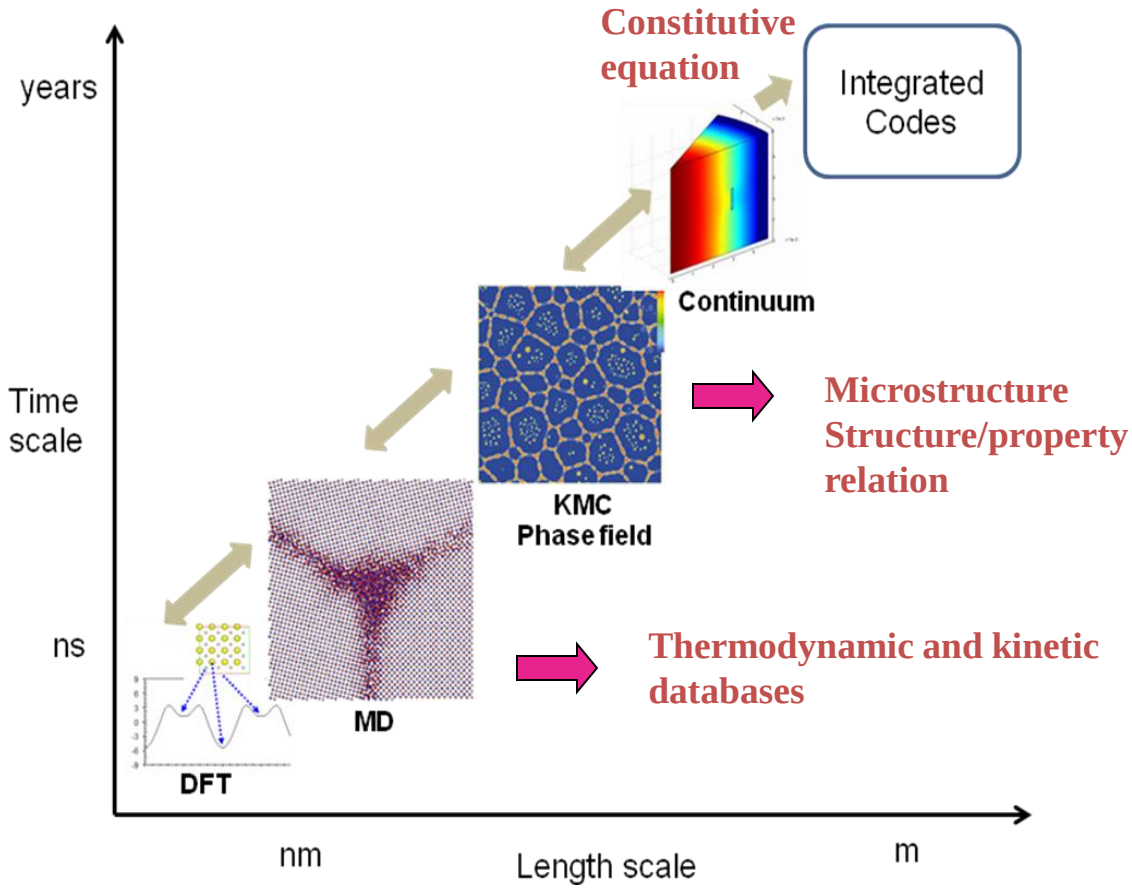
High energy recoil can damage structure.
Disordered structure is mechanically weaker and will leach more.
Combined effects of radiation, stress and temperature.
Can we use computation to understand radiation tolerance?

Supercomputers to the rescue



Tremendous growth in computing power.
Source: singularity.com

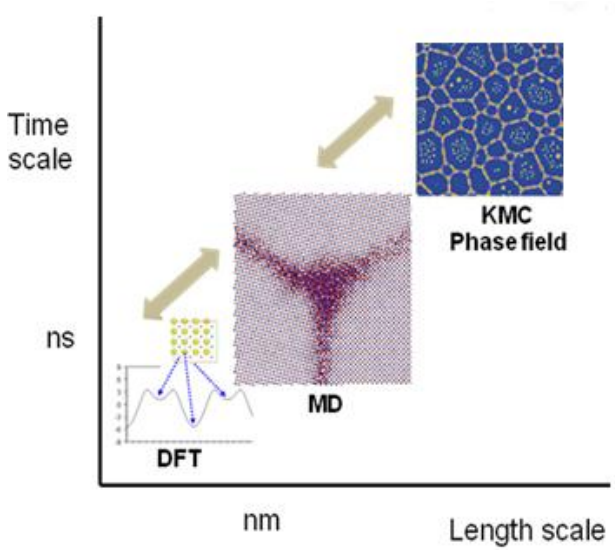
Hierarchical Modeling



IPSC	Our task
Waste Forms & Systems	X
VV & UQ	X

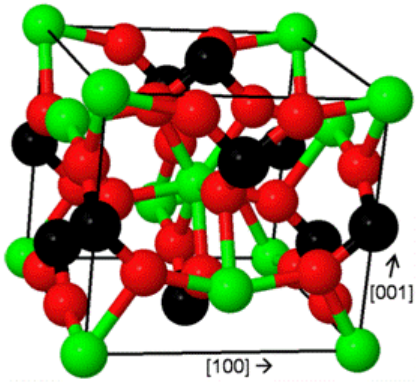
Verification and Validation is Important

- Develop potentials to describe how atoms interact
- Fit parameters of potential based on experiment and electronic structure calculation.
- Use potentials in MD simulations and pass information to next higher level.
- Verify and validate against experiment at each level (with Peter Schultz et al at Sandia)
- We will demonstrate this approach for Xenotime
- Previous work on Zircon

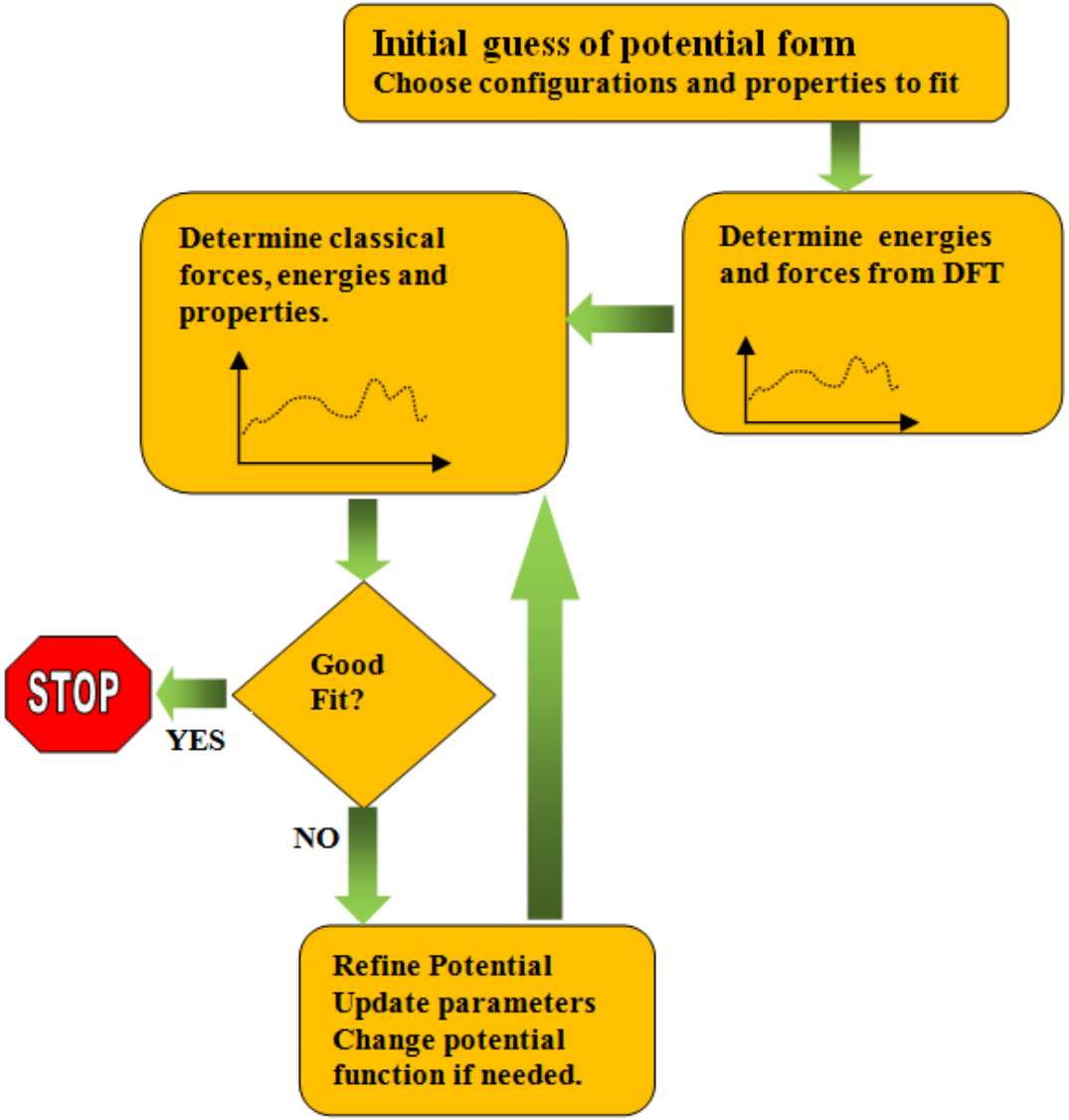


Zircon vs. Xenotime

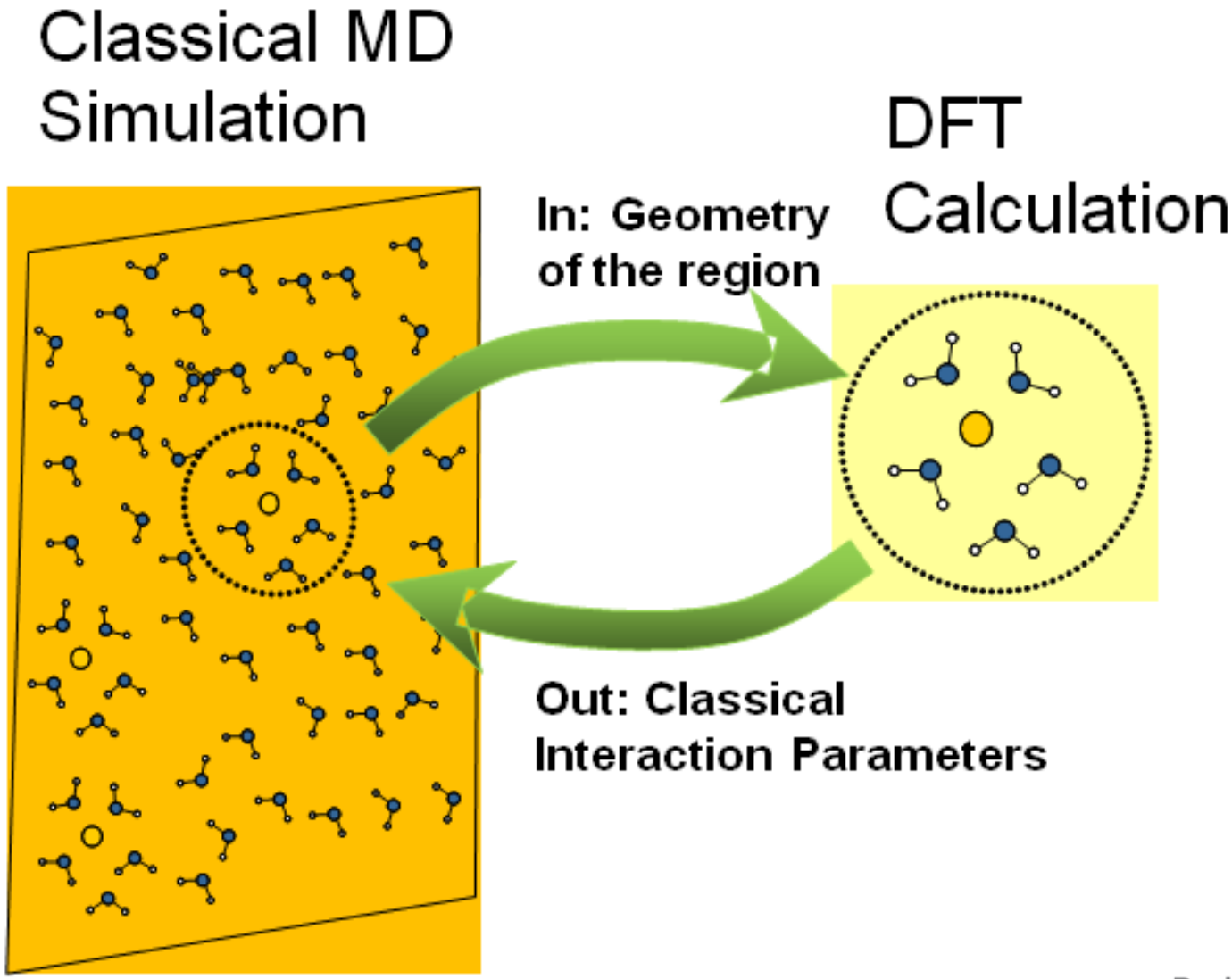
- Zircon ($ZrSiO_4$) is a durable mineral that occurs worldwide
- Found with U and Th typically 5000 ppm (but even a few %)
- It is used by geologists to determine the age of rocks (U-Pb radiometric dating, fission tracks etc). Some rocks have been dated to 4.4 billion years and they tell us about water on Earth's surface at that time.
- They are also used as inexpensive gemstones
- It is a candidate for locking up actinides
- Phosphates appear to be better waste forms compared to silicates. Why?
- We will compare rad. damage in YPO_4 to that in $ZrSiO_4$
  - First, we need to develop potentials for YPO_4
  - Then, we need to validate the potentials



Algorithm for potential development

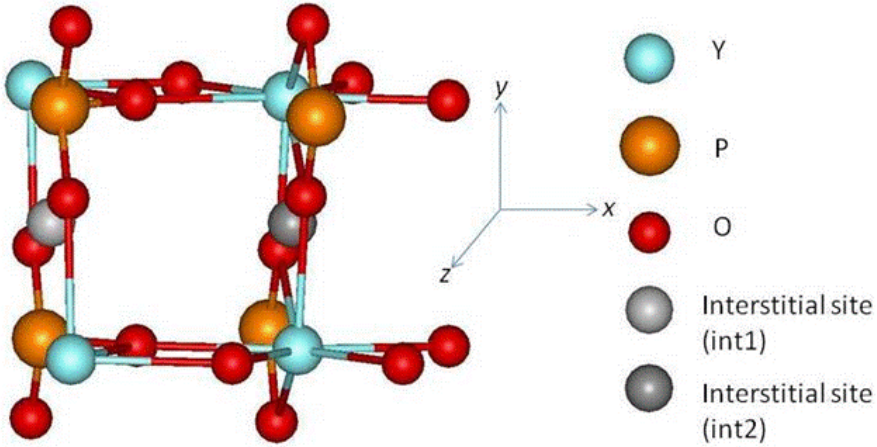


Long term vision: QM/MM scheme



Defect energies in YPO_4

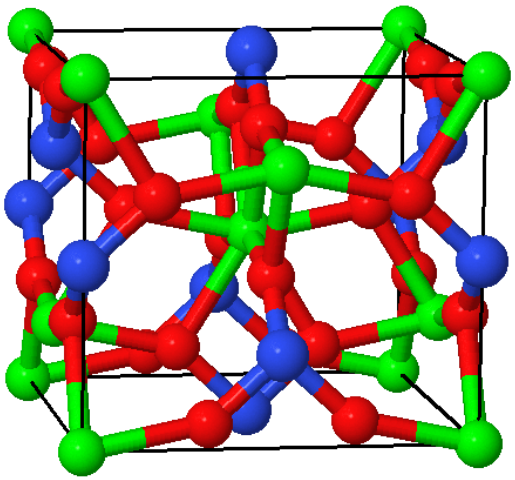
Defects	Defect formation energy (eV)
Vacancies	
Y_{vac}	15.09
P_{vac}	17.94
O_{vac}	14.29
Antisite defects	
Antisite pair	12.66
Y_P	6.22
P_Y	10.06
Interstitials	
Y_{int1}	11.39
Y-Y splitting toward int1	11.55
Y_{int2}	7.75
P_{int1}	9.24
P-P splitting toward int1	10.53
O_{int1}	3.39
O-O splitting toward int1	2.53
O_{int2}	4.36
O-O splitting toward int2	2.53
Frenkel pairs	
$Y_{vac}+Y_{int1}$	48.68
$Y_{vac}+Y_{int2}$	28.18
$P_{vac}+P_{int1}$	19.56
$O_{vac}+O_{int1}$	11.42
$O_{vac}+O_{int2}$	12.01



DFT calculation with VASP
GGA
Plane wave basis set (PW91)
Cutoff energy 500 eV
2x2x2 super cell (192 atoms)

Interatomic potential for YPO_4

Property	Potential	Experiment
Lattice constant *a* (Å)	6.895	6.883
Lattice constant *c* (Å)	6.029	6.021
C_{11} (GPa)	220	220
C_{12} (GPa)	28	55
C_{13} (GPa)	93	86
C_{33} (GPa)	337	332
C_{44} (GPa)	65	65
C_{66} (GPa)	17	17



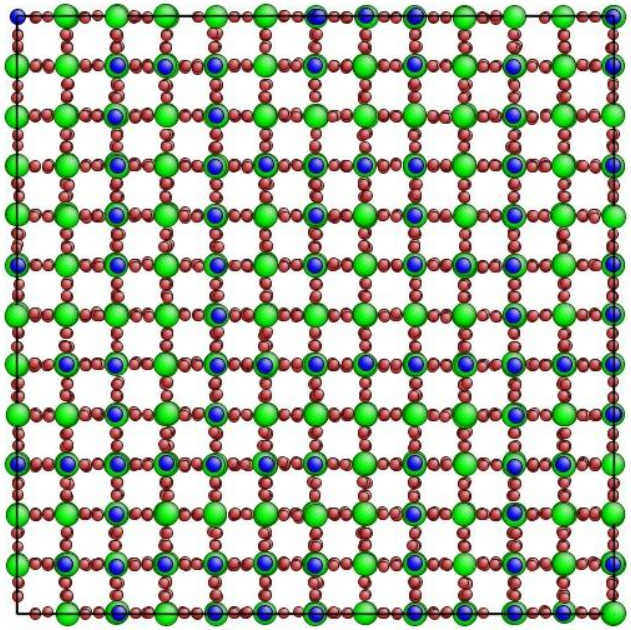
Potentials were fitted to experimental data.
Further refinement underway based on DFT data.

The fit is good so far.

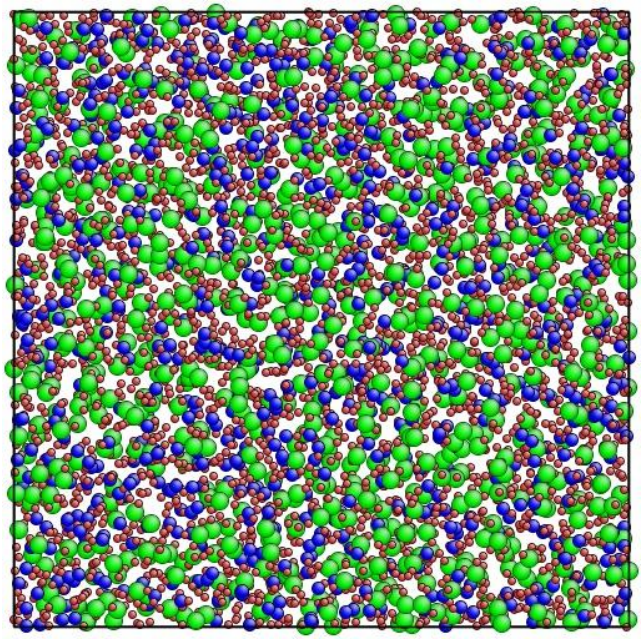
Interatomic potential for $ZrSiO_4$

- Tools available for simulating both structures and mechanical properties of $ZrSiO_4$, ZrO_2 and SiO_2 are extremely limited.
- Unified force field to model properties of different phases of $ZrSiO_4$, ZrO_2 and SiO_2: Crystal and amorphous

Crystal



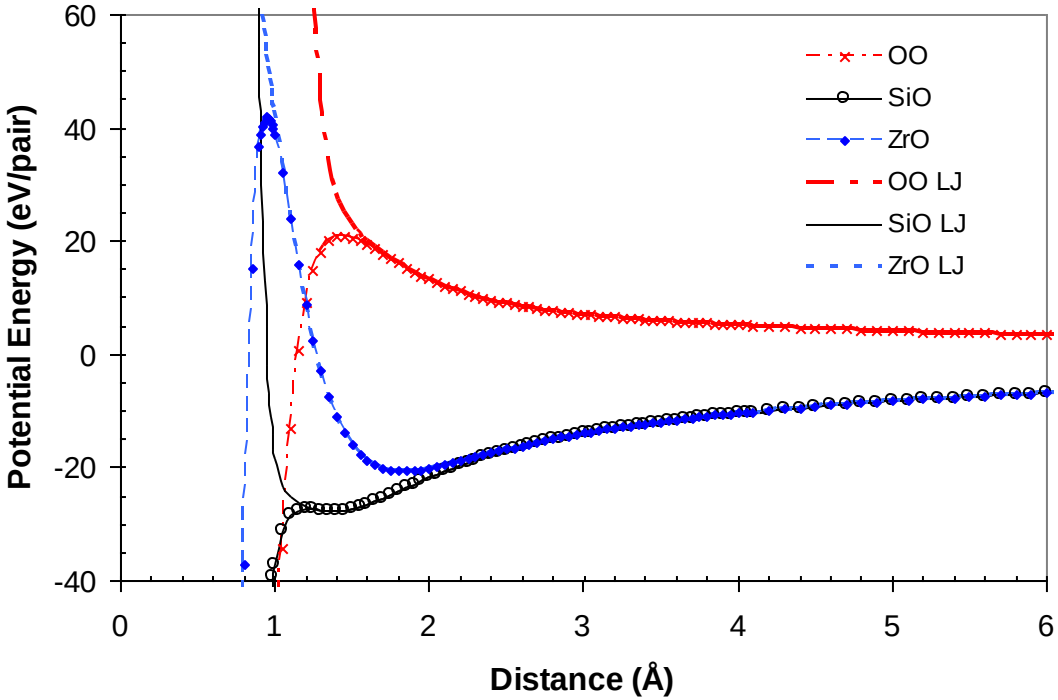
Amorphous



Function form of potential for $ZrSiO_4$

$$\phi(r_{ij}) = q_i q_j / r_{ij} + A_{ij} \exp(-r_{ij} / \rho) - \frac{C_{ij}}{r_{ij}^{\,6}}$$

$$\phi(r_{ij})^m = \phi(r_{ij}) + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{18} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



J. Yu et al, Journal of Materials Chemistry **19(23)** (2009) 3923-3930.

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Fit to the properties of $ZrSiO_4$

	Zircon		Reidite	
	This work	Expt	This work	Expt./DFT
Lattice (Å)				
a	**6.56**	6.60	**4.79**	4.73
c	**6.14**	5.98	**10.45**	10.51
V ($Å^3$)	**264.3**	260.8	**239.3**	235.5
B (GPa)	**241**	225	**231**	301
Elastic (GPa)				
C_{11}	**455**	424	**495**	470
C_{33}	**436**	490	**317**	288
C_{44}	**96**	114	**85**	74
C_{66}	**64**	49	**146**	133
C_{12}	**119**	70	**205**	241
C_{13}	**146**	150	**131**	255
E ($eV/ZrSiO_4$)	**-104.73**		**-104.47**	

J. Yu et al, Journal of Materials Chemistry **19(23)** (2009) 3923-3930.

Zircon was fitted. Reidite was not fitted.

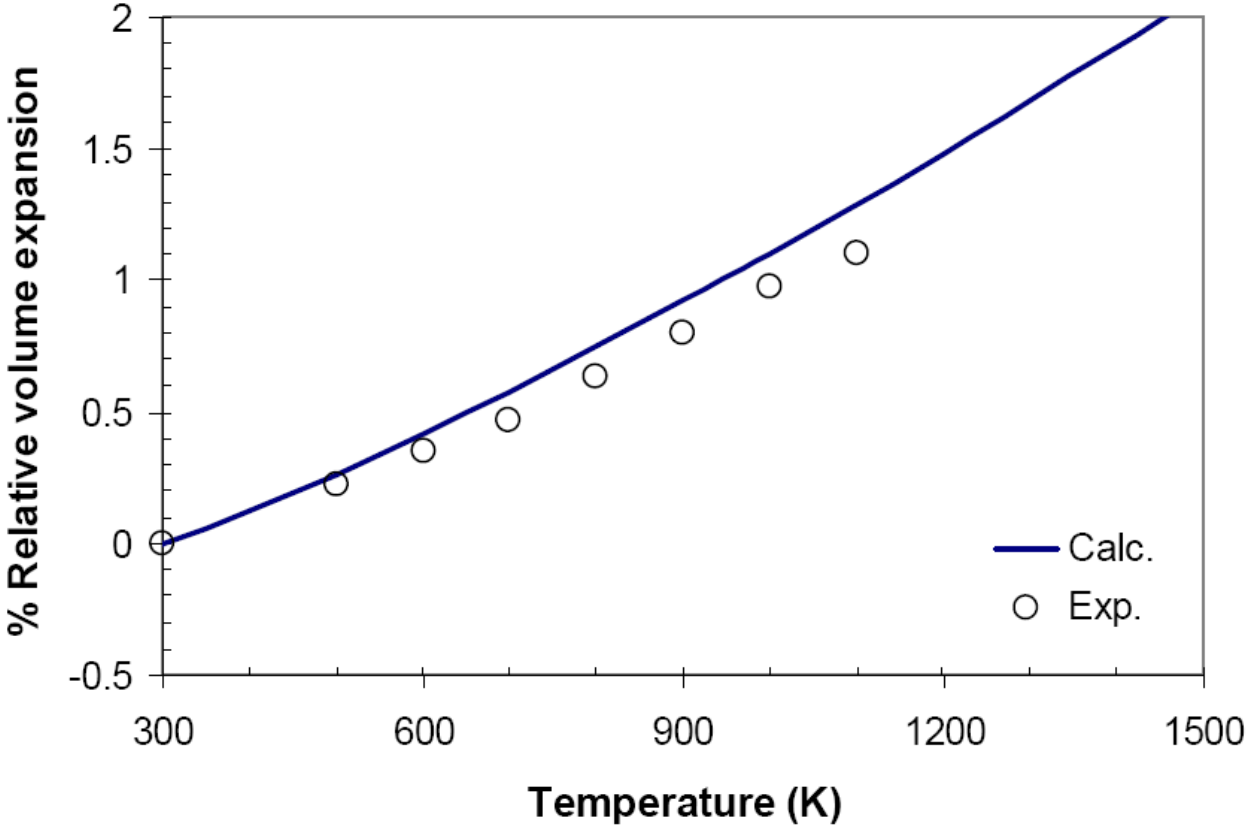
Fit to the properties of ZrO_2

	Monoclic		Cubic	
	This work	Expt	This work	Expt
Lattice (Å)				
a	**5.19**	5.15	**5.12**	5.09
b	**5.25**	5.21		
c	**5.29**	5.31		
V ($Å^3$)	**142.6**	140.9	**134.2**	131.9
B (GPa)	**151**	172	**254**	167
Elastic (GPa)				
C_{11}	**338**	362	**599**	417
C_{33}	**233**	258	**599**	417
C_{44}	**105**	100	**80**	47
C_{66}	**147**	126	**80**	47
C_{12}	**174**	142	**82**	82
C_{13}	**55**	55	**82**	82
E (eV/ZrO_2)	**-46.133**		**-46.021**	

J. Yu et al, Journal of Materials Chemistry **19(23)** (2009) 3923-3930.

ZrO_2 was not fitted.

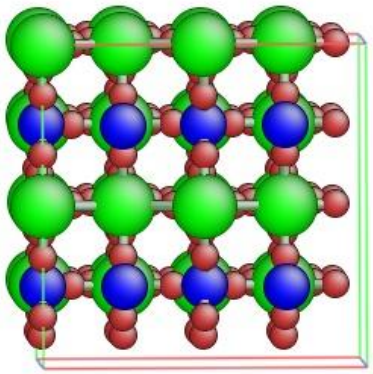
Thermal expansion of $ZrSiO_4$



J. Yu et al, Journal of Materials Chemistry **19(23)** (2009) 3923-3930.

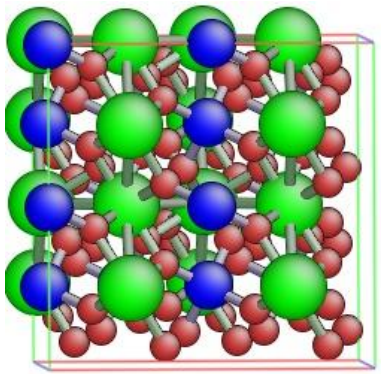
Further validation of potential for $ZrSiO_4$

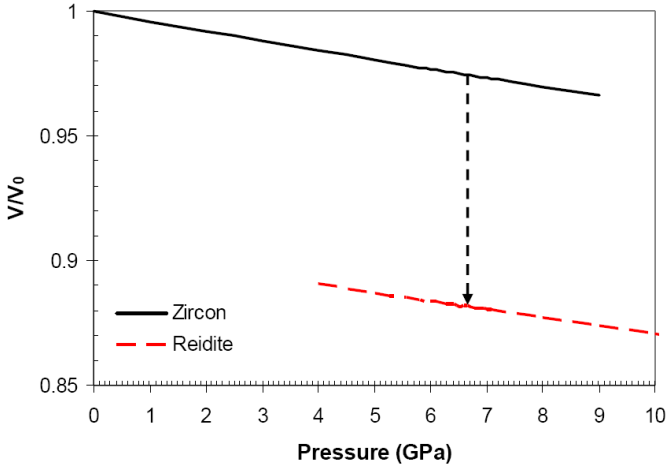
Zircon

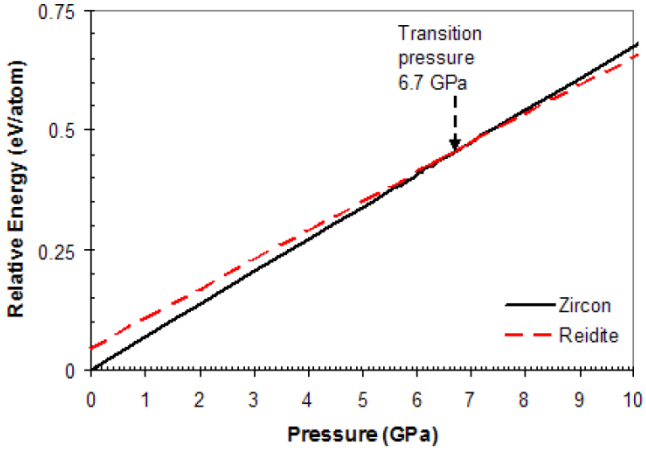


Pressure

Reidite

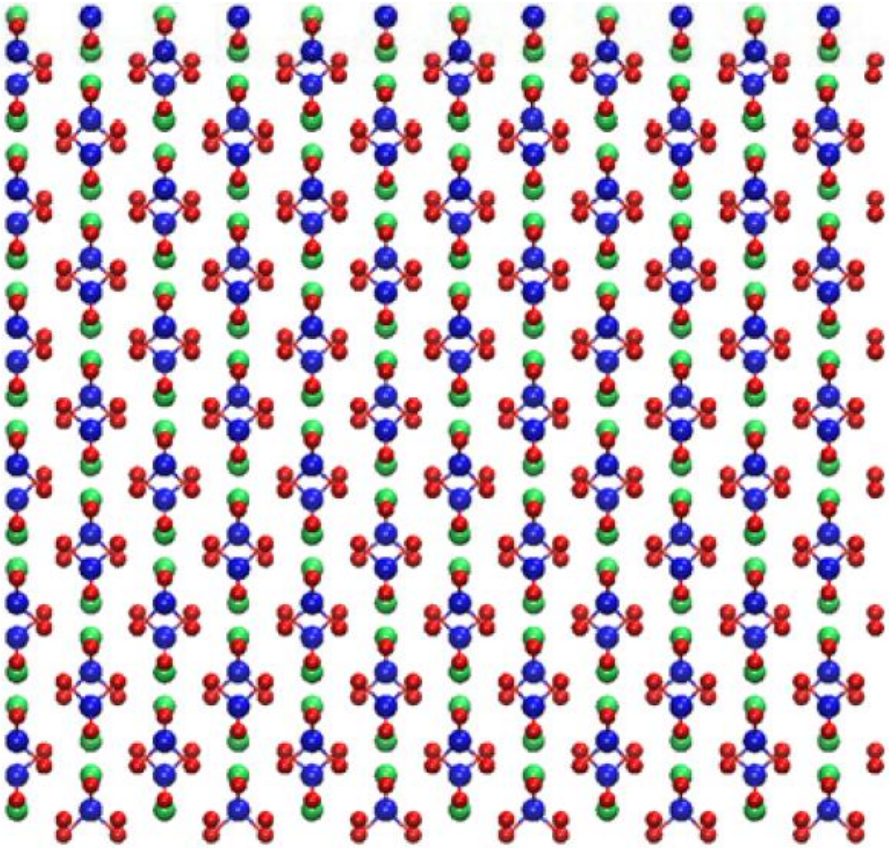


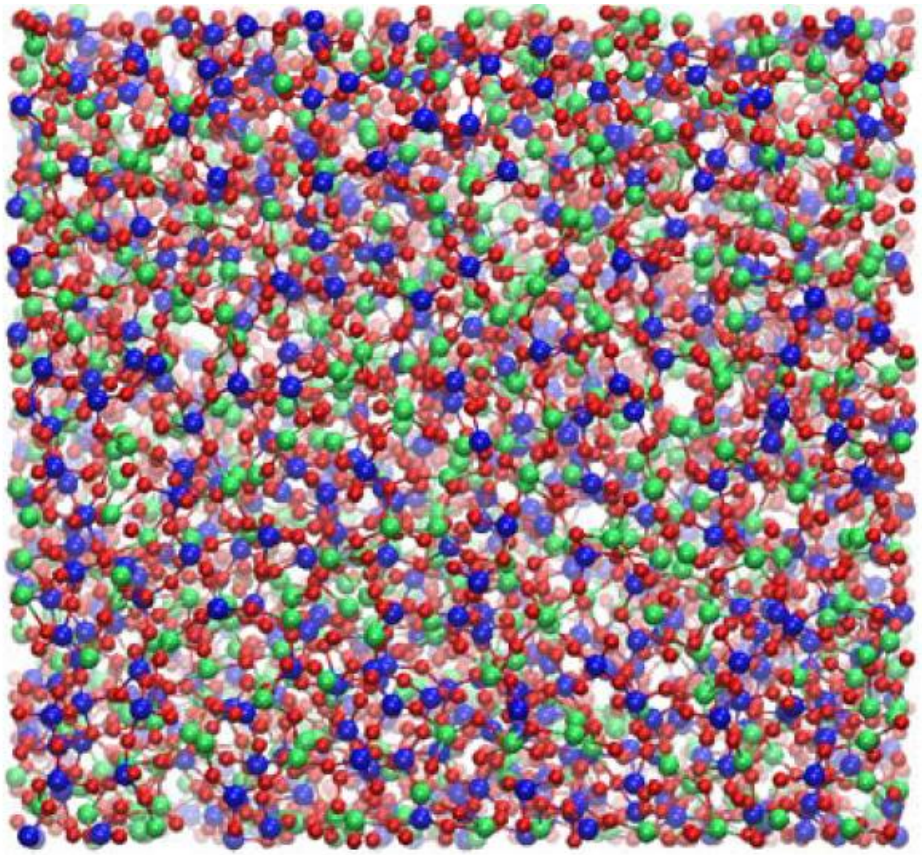




Expt. < 10 GPa S. Ono, et al, *American Mineralogist*, **89**, 185 (2004)
DFT: 5.3 GPa M. Marques, et al, PRB, **74**, 014104 (2006)

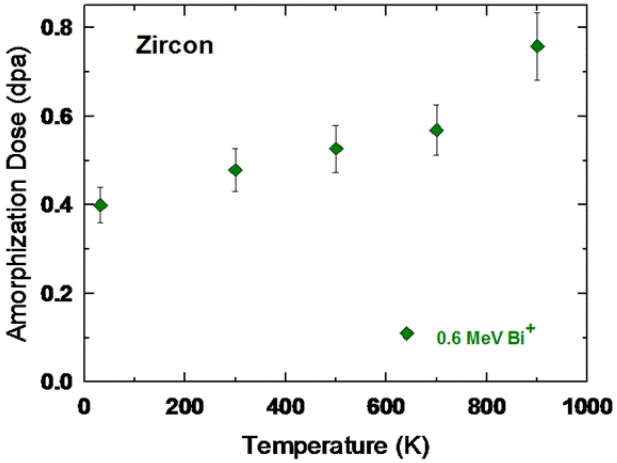
Crystal → Amorphous Transformation

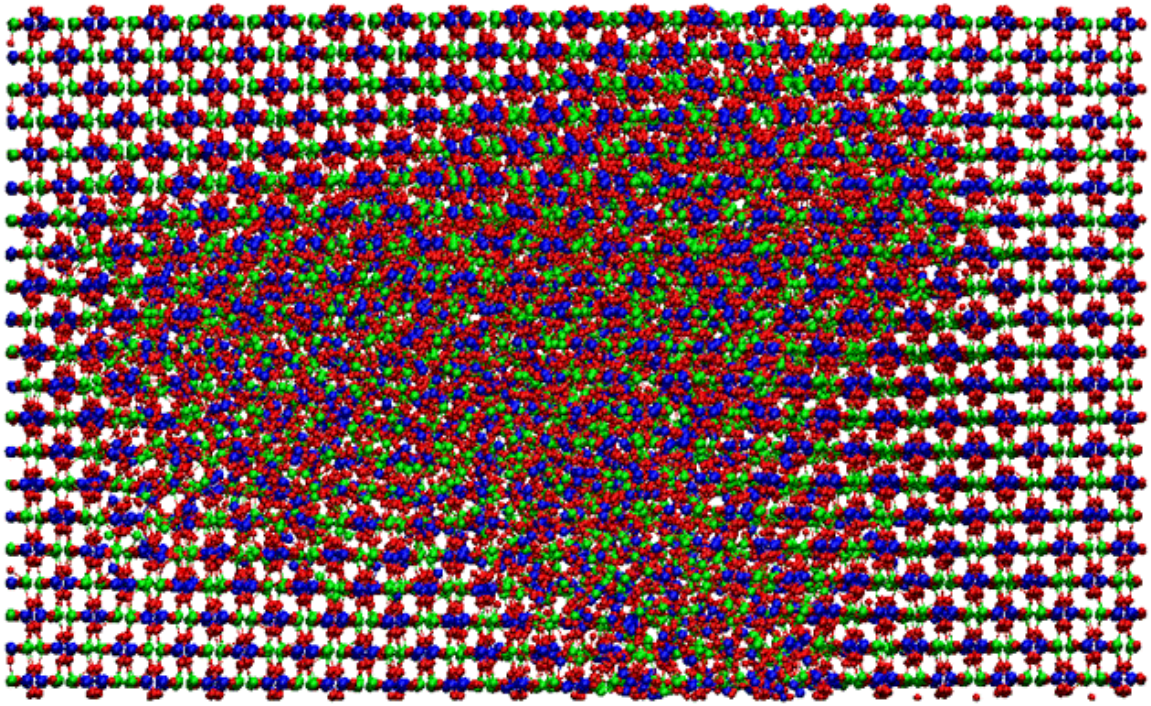




Volume expansion and phase separation in accord with experiment.

Zircon is readily amorphized by heavy ions

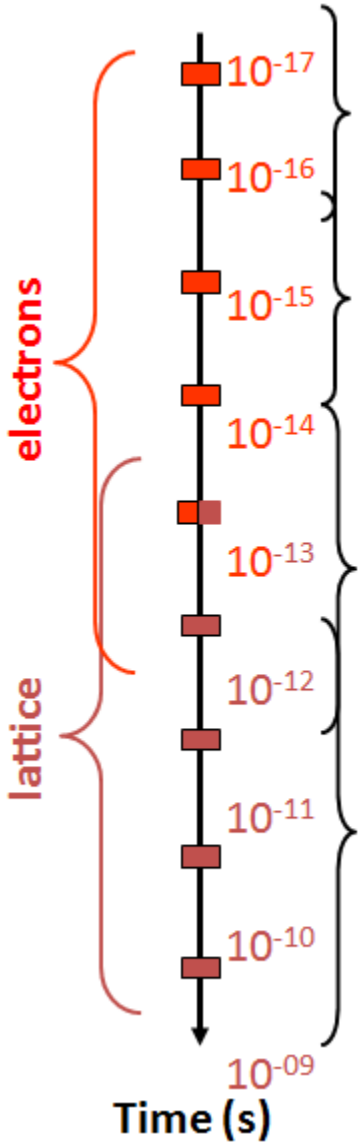




115 Å x 70 Å section of $ZrSiO_4$ simulation cell following a 30 keV U recoil along [001] at 300 K.
Unequal-charge model + ZBL; NVE ensemble
Zr becomes under-coordinated; Si is polymerized

Direct impact amorphization in the displacement cascade.

Modeling Electronic Energy Loss Processes

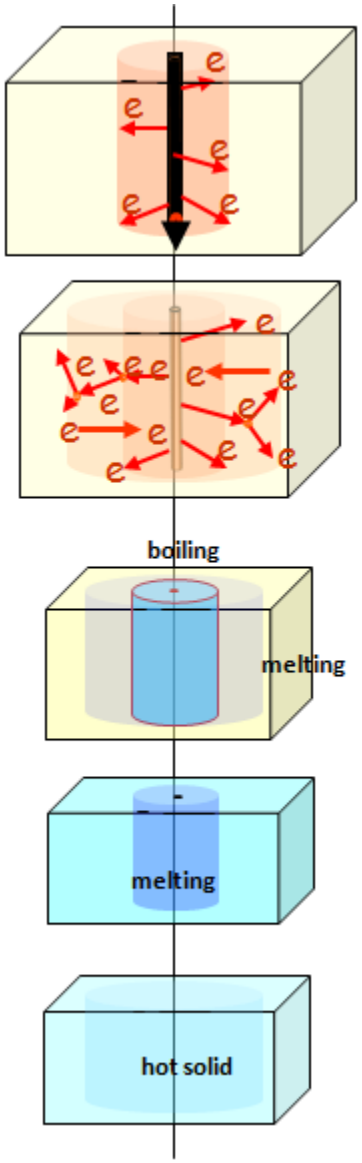


Stage 1 :Energy loss: electrons (e)
- generation of δ-electrons
- creation of a Coulomb field

Stage 2 : plasma formation
- kinetic electron relaxation
- ionizations
- electron cascades
- screening of Coulomb field
- electron T relaxation

Stage 3 : energy transfer to lattice
- electron-phonon coupling
- temperature rise
- shock wave generation

Stage 4 : lattice processes
- Thermal spike and cooling
- Radiative decay
- e-hrecombination
- pressure relaxation
- phase transformation



Processes:
Fission
Swift heavy ions

Possibilities:
- Synthesize new phases
- Take system far from equilibrium
- Study radiation tolerance
- Understand electron-phonon coupling

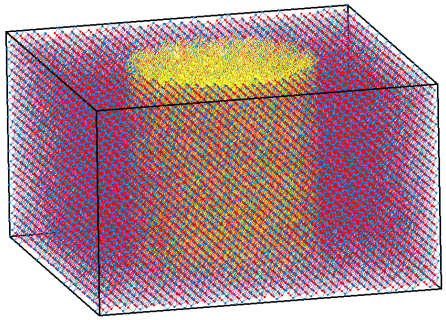
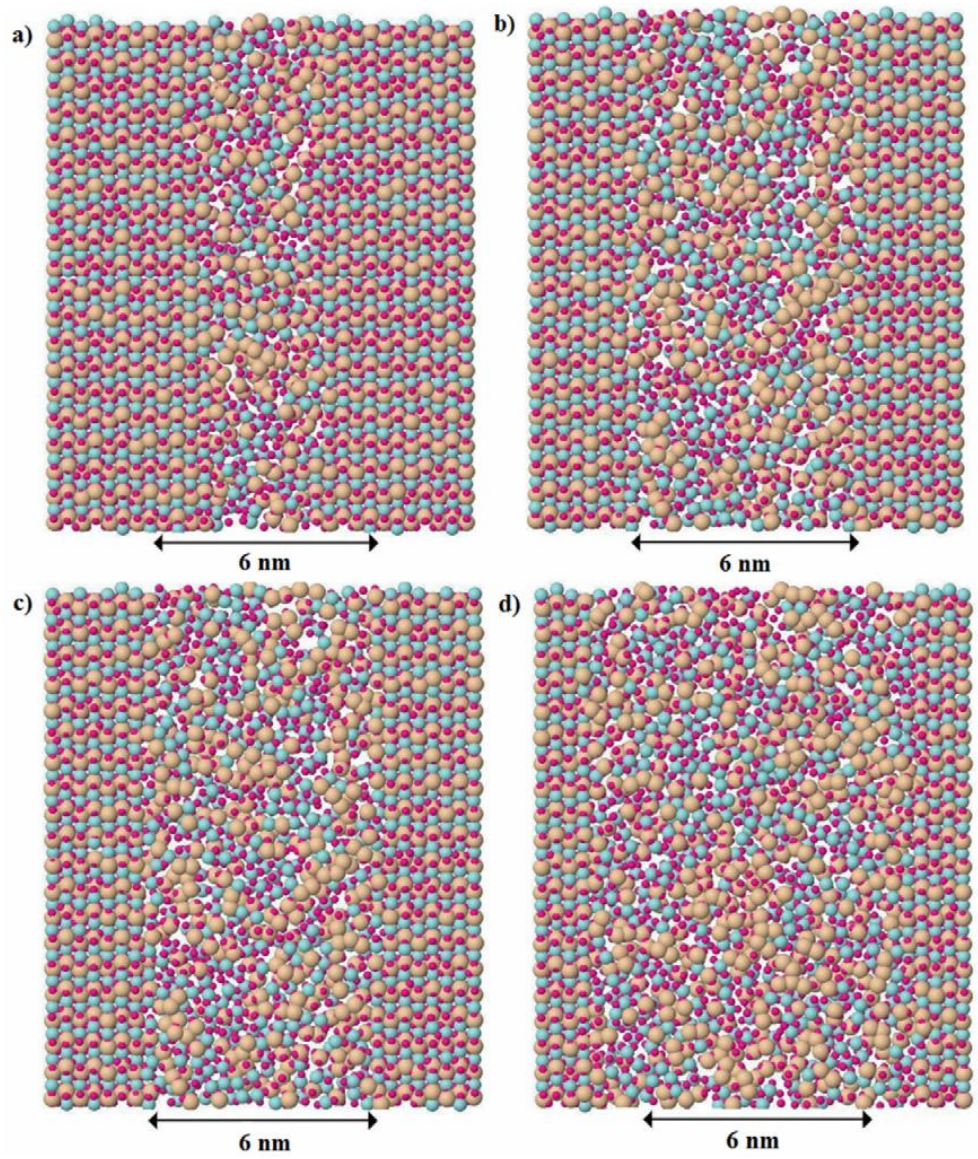


Image courtesy of Marcel Toulemonde

Swift Heavy Ion Damage in Zircon



a) 3.9 keV/nm
b) 5.9 keV/nm
c) 7.7 keV/nm
d) 12.8 keV/nm

Track size increases with energy deposition.

No track below 3.9 keV/nm.

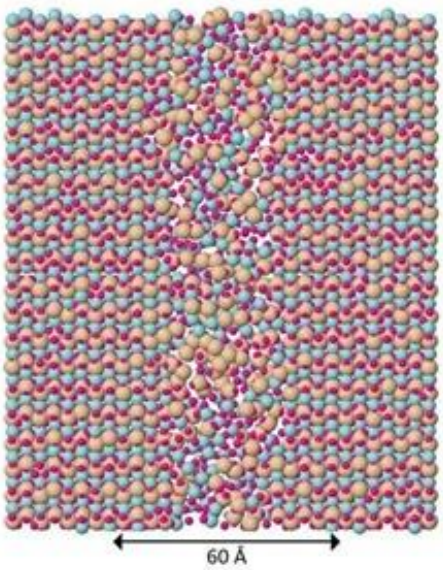
Swift Heavy Ion Damage in Zircon

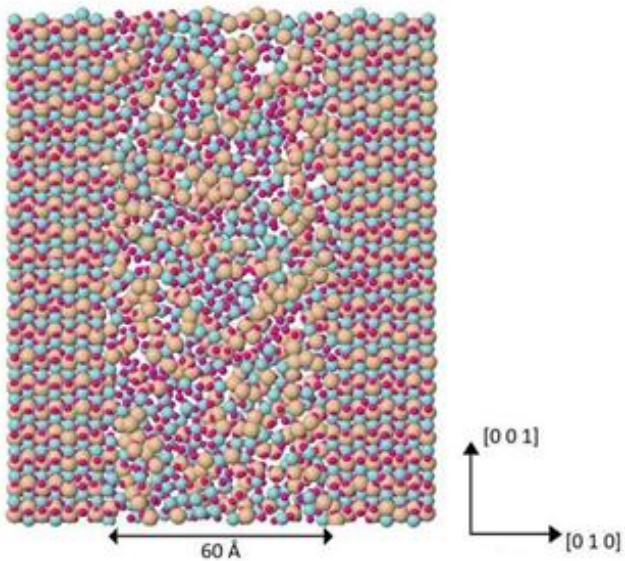
Zircon: 4 keV/nm 6 keV/nm

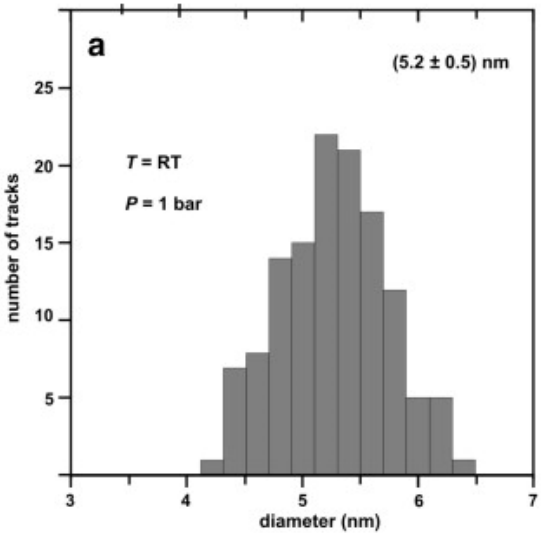
P. Moreira et al, JPCM 22 (2010) 395008

Expt. 21 keV/nm (10 GeV Pb)

M. Lang et al, EPSL 274 (2008) 355.







Simulations provide insights into experiments.
We can estimate electron-phonon coupling efficiency by comparing experiment and simulation.

Progress

1: Developed inter-atomic potential for YPO_4 with Cambridge U.

Limited experimental data. How do we validate this potential?

We have fitted equilibrium properties.

We are calculating melting point and expansion coefficient.

DFT calculations for defect energies are ongoing

2: Methodology of potential development is being documented

How do you choose a functional form?

Buckingham (ionic)/Morse (ionic + covalent)

Should we include shells for ionic polarizability? Cost?

How many parameters are enough?

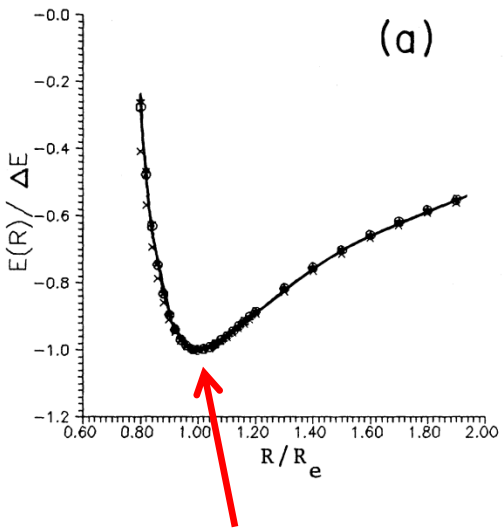
What should be the range of the potential?

What properties should we fit? Where do we get them from?

Should we fit to just one point on the PE surface?

How do we decide that the fit is good enough?

Test the potential with multiple codes?



We are developing <u>guidelines</u> for fitting potentials.

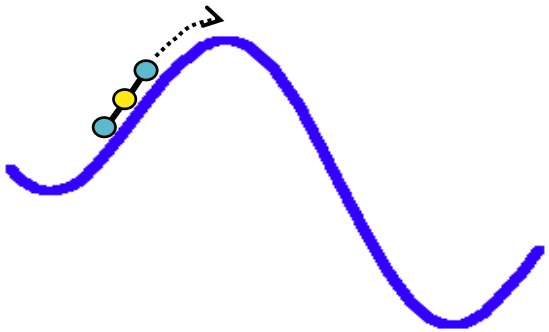
Long-Time Dynamics Based on Dimer Method

MD calculations

- Simulating at different temperatures – from 200 to 1200 K, depending on problem
- Evaluating mean square displacements at each temperatures
- Diffusion coefficient - $\ln(D) = \ln(D_0) - \frac{E_m}{k_B T}$

Long time dynamics based on the dimer method

- There may be more than one saddle point separating two energy basins.
- The dimer method – searching all possible transition states.
- Nudged elastic band methods can find the most direct routes, but not necessarily the most energetically favorable paths – needs start and end states



➢ Long time dynamics = dimer method + kinetic Monte Carlo method

Predictive Multi-scale Models for Fuels

Linking atomistic dynamics ←→ continuum models

Information passing:

1. Free energy as a function of defect and impurity concentration
2. Defect generation rate and defect + impurity distribution
3. Reaction rates of defects and impurities (recombination, binding …)
4. Nucleation of voids and bubbles (critical size as function of T)
5. Mobility of defects as a function of defect distribution and T

We are working to demonstrate the validity and utility of this approach in Ceramic Waste Forms and Glasses

Summary

- Computer simulations are valuable for studying fundamentals of rad. damage
- There can be large uncertainties when projected to long time scales
- We are developing procedures to verify and validate our methods at every stage against more accurate (lower scale) models and experiment
- Run the same calculation with multiple codes and computers to determine one class of uncertainty
- Develop linkages between scales and verify their validity
- Train students and Postdoctoral researchers
- Collaborating with US universities and UK researchers

Research funded by US DOE, NEAMS program