Nuclear Materials from Experiments and Atomistic Simulations

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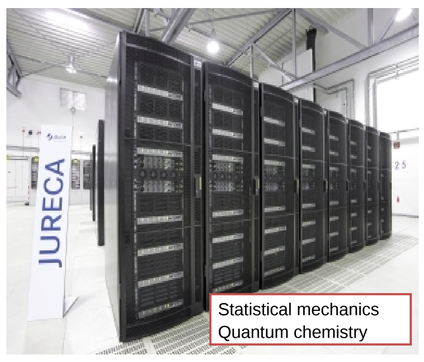
Majority of HLW (**H**igh **L**evel Nuclear **W**aste) consists of directly stored UO_2-based spent nuclear fuel or its vitrified form. In order to provide a solid scientific basis of nuclear waste management and disposal we try to understand the molecular-scale originating properties of various relevant nuclear materials, including waste and waste forms, and their long-term performance. In this contribution, we report the results of joint atomistic modeling and experimental studies of HLW related materials such as nuclear glass and Cr-doped UO_2-based model systems.

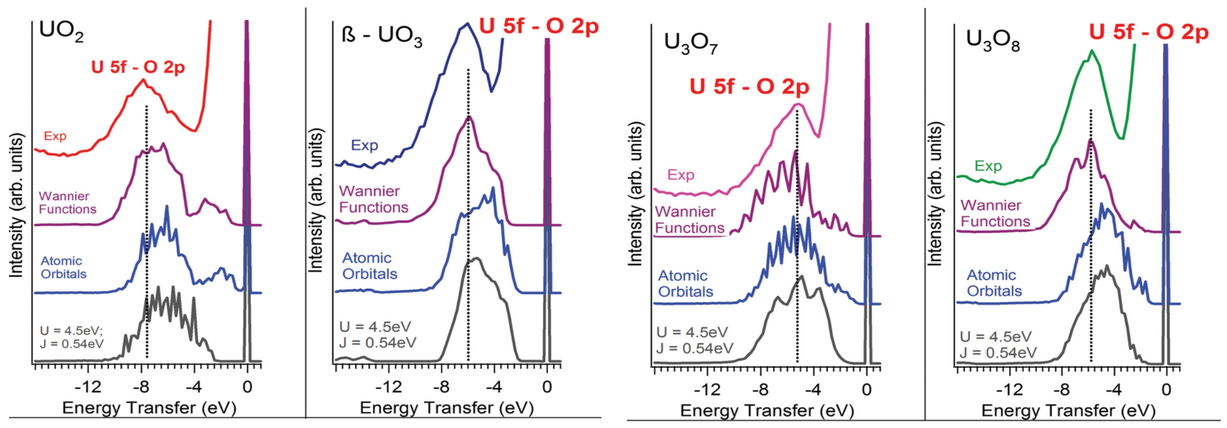
Atomistic simulations

In our work we apply a variety of atomistic modeling methods. The simulations of glasses are performed with the method of classical molecular dynamics. Here we apply force fields[1] to describe the interactions between atoms. We use LAMMPS and GULP codes[2] for that purpose. The simulations of solid phases are based on *ab initio* Density Functional Theory (DFT). For *f*-elements we use the DFT + *U* method but with the Hubbard *U* parameter values derived from first principles using the linear response method[3-4].



Atomistic simulations and thermodynamic modeling

Simulations of mixed uranium-oxides



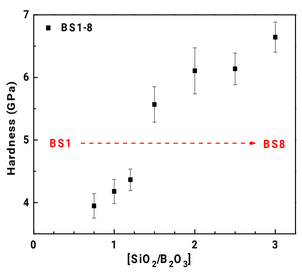
UO_2-based materials could undergo structural and chemical change. In new phases U(IV) could oxidise from U(IV) to U(VI), producing the risk of fast dissolution. Here by combination of HR-XANES and atomistic simulations we investigate electronic structure of mixed uranium-oxides[8]. The best match to the experiment is obtained with DFT+*U* method, the derived Hubbard *U* parameter and Wannier representation of *f* orbitals.

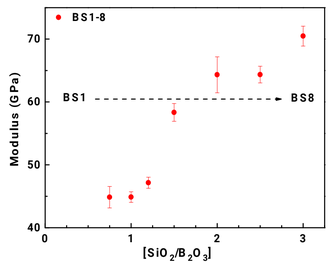
Simulations of borosilicate glasses

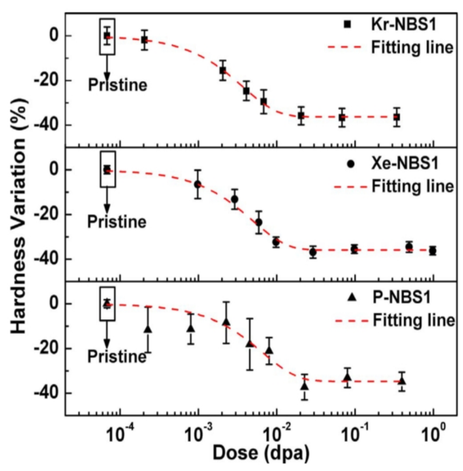
Measurements of Young's modulus and Hardness by nano-indentation[5-6]

Tab. 1 The compositions of BS1-8

Mol%	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8
SiO_2	37.7	44.0	48.0	52.8	58.7	62.9	66.0	68.4
B_2O_3	50.3	44.0	40.0	35.2	29.3	25.1	22.0	19.6
Na_2O	12.00							







Results:

- Increase of Young's modulus and Hardness with Si content.
- Measurements of change of Young's modulus and Hardness under irradiation.
- Clear decrease in Hardness, amorphization at ~0.1 dpa.

Experimental data from [5-6]

Open question: What causes the observed change?

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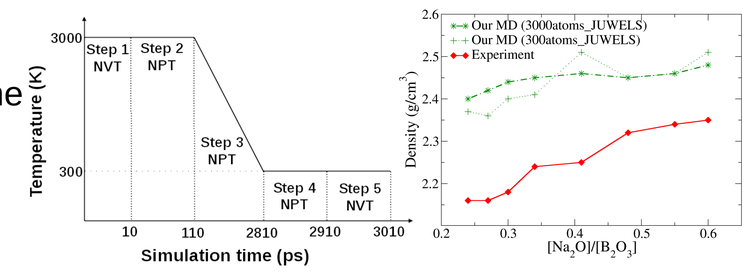
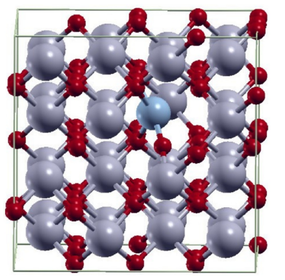
- we try to answer this with the
- aid of atomistic simulations



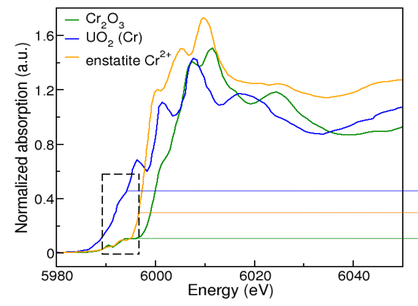
Simulations of Cr-doped UO_2

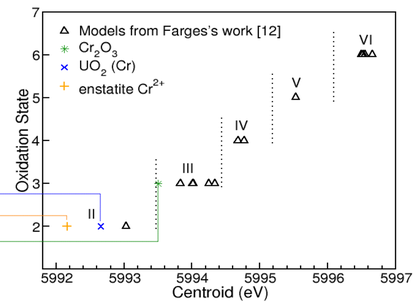
Addition of Cr to UO_2 enlarges the grain sizes and improves the performance of the nuclear fuel(e.g. by limiting fission gas release). We want to understand how Cr is incorporated into the bulk-UO_2 and in which oxidation state. Is it Cr(III) as claimed by experimental studies[9]?



Tab. 2 Relative lattice parameter In Cr-doped UO_2

Configuration	$\Delta a/a$ ($\times 10^{-3}$)
1Cr	-1.72
2Cr+1Ov	-1.41
1Cr+1Ov (a)	-0.25
exp.[10]	-0.12
exp.[11]	-0.22



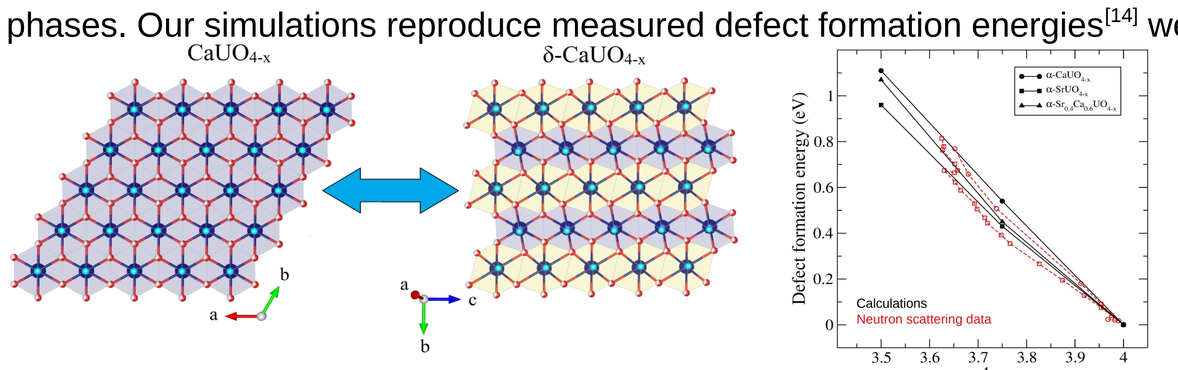


- DFT+U simulations show that Cr incorporates as Cr(II) and the charge is balanced by O vacancies or formation of U(V).
- The thermodynamically favorable structure composes of associated pair of Cr(II) atom and O vacancy (neighboring site).
- XANES is used to judge the oxidation states of elements (*e.g.* Cr in UO_2).
- The re-evaluation of the experimental XANES data shows presence of Cr(II).
- This structure fits the experimental data: Cr solubility, XANES and change in lattice parameter.[13]

Simulations of MUO_{4-x} (Secondary phases)

Good description of defects and their formation

We investigate *T*-driven O-defects formation & phase transformation in MUO_{4-x} phases. Our simulations reproduce measured defect formation energies[14] well.

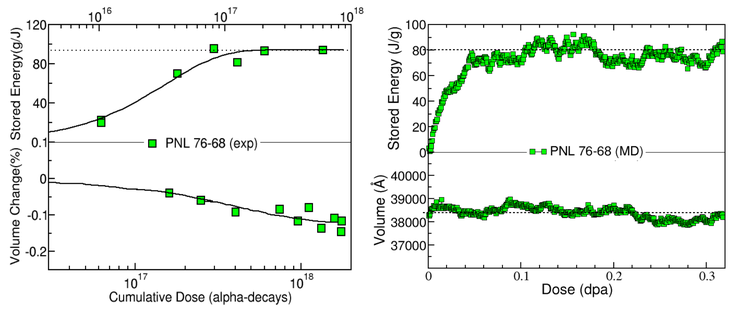


An intriguing thing is ordering of $SrUO_{4-x}$ compound at high T shown by the formation of super-lattice reflection[14].

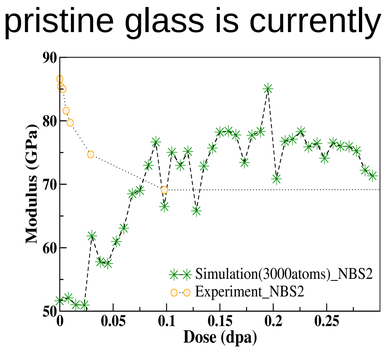
Test case: Simulations correctly predict stored energy and volume change of PNL 76-68 glass[7]

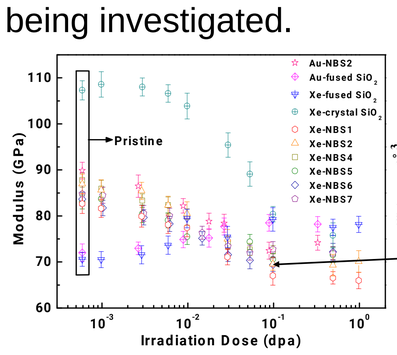
- Stored energy is very close
- Volume change is negligible

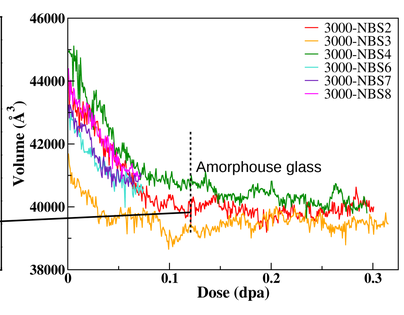
Experimental data from [7]



Simulations correctly predict the critical amorphization dose at ~0.1 dpa and Young's modulus of irradiated NBS glass. Reason for discrepancy observed for pristine glass is currently being investigated.







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