Atomistic simulations of nuclear waste materials

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Aims

- Simulations of radiation damage processes in ceramic nuclear waste forms (monazite).
- Derivation of heat capacity for xenotime-type ceramics ($Ln PO_4$, Ln=Tb,...,Lu).
- Calculations of structural and thermophysical properties of pyrochlore-type ceramics ($A_2B_2O_7$).

Results

Computational details

- Molecular dynamics simulations with LAMMPS code and Buckingham-type interaction potentials. The potentials parameters were fitted to the *ab intio* data. And the unit cell contains 1536 atoms.
- Quantum-ESPRESSO and CPMD DFT packages, Vanderbilt ultrasoft pseudopotentials for *ab initio* simulations and plane-wave energy cutoff of 50 Ryd.

Monazite-type ceramics

- **Good nuclear waste form candidate:** natural monazite minerals contain significant amounts of Th and U (up to 27%) without any significant indication of radiation damage. These minerals are often billions of years old.
- High potential waste load and chemical durability.
- Investigated within the BMBF "Conditioning" project.

Threshold displacement energy

Using molecular dynamics method we simulated the threshold displacement energies E_d - the minimum kinetic energy required to displace an atom from its lattice site - and the related atom displacement probabilities.

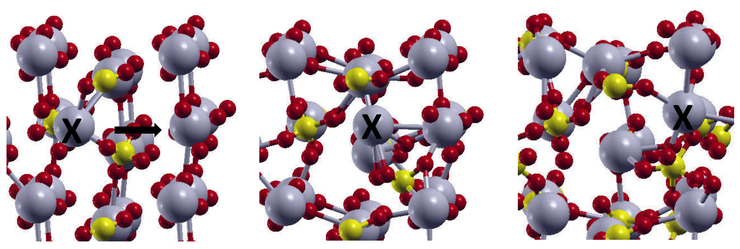

Fig. 1. Creation of the *Ln*-cation displacement in monazite by application of initial velocity (illustration of the simulation method).

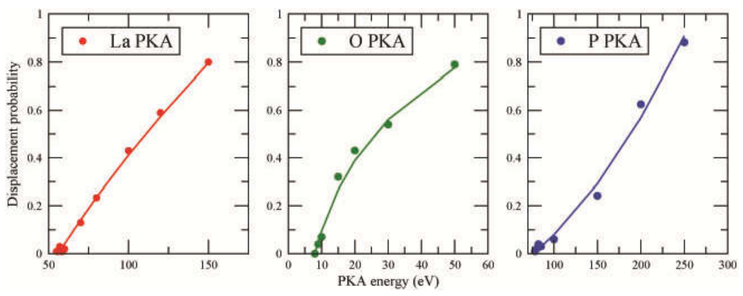

Fig. 2. The simulated atomic displacement probabilities of La, P, O PKA in $LaPO_4$ at T=300K [1]

- These E_d values are different with generic data sets.
- The derived E_d value have been used for simulations of the radiation damage extend and defects accumulation in monazite-type ceramics, which provided the information on optimal conditions for experiments [1].

Correlation between displacement probability and dissolution rate

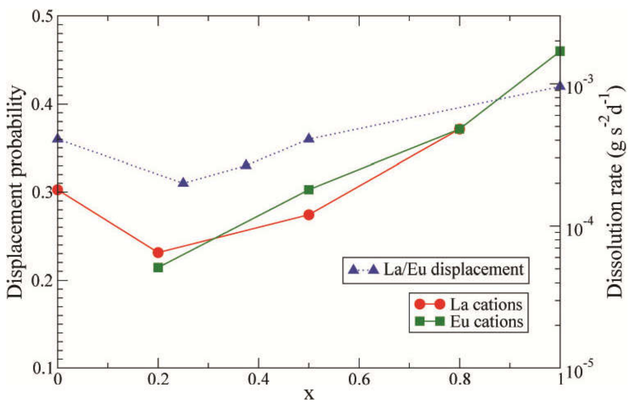

Fig. 3. The atomic displacement probability of $La_{1-x}Eu_xPO_4$ solid solution (left y-axis) [3] and the normalized steady-state dissolution rates measured for $La_{1-x}Eu_xPO_4$ solid solution and calculated from the released Eu and La concentrations [2] (right y-axis).

- There is a minimum in displacement probability of $La_{1-x}Gd_xPO_4$ solid solution at x~0.2, which correlates with the minimum observed in the dissolution rates [2,3].

Temperature dependence

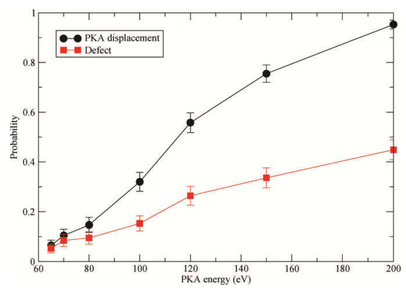

Fig. 4. The displacement probabilities (DP) and the defect formation probabilities (DFP) for the La PKA at 300 K.

- Many initial displacements resulted in fast recombination of the defects also through cation replacements.

Amorphization

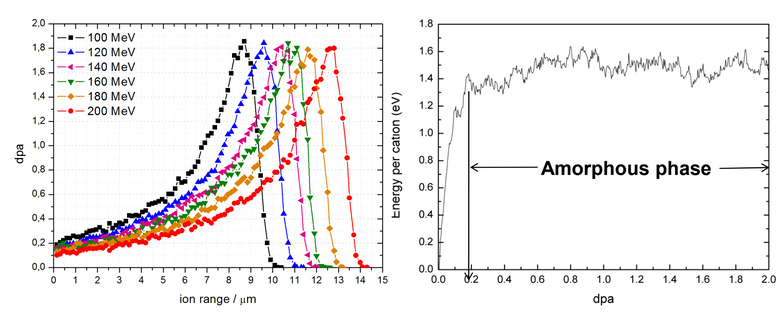

Fig. 5. Left: simulation of radiation damage: Au on $LaPO_4$, simulated by Dr. Andre Filby, Dr. Ralf Kunz and Dr. Thomas Moeller (BRENK GmbH, Aachen) using Ed we calculated. Right: simulation of critical amorphazation dose.

- Atomistic simulations provide information on the critical amorphization dose (~0.2 dpa for $LaPO_4$ monazite) and allow for prediction of the extend of the radiation damage given bombarding particles type and energy. It is very close to the experimental value of 0.3 dpa for monazite [4].

Xenotime-type ceramics

- Understanding the variation of heat capacities of $Ln PO_4$ xenotime (zircon structure).
- Providing data on the heat capacities for unmeasured $Ln PO_4$ xenotime compounds.

Heat capacity

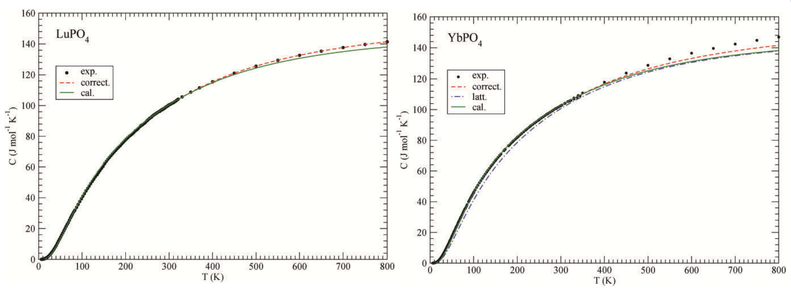

Fig. 6. The calculated and measured heat capacity of $LuPO_4$ and $YbPO_4$ [4].

- The calculated values match the experimental data well.
- There is a significant contribution to the heat capacities from the thermal excitations of *f*-electrons (Schottky contribution) [5].

Collaborators:

Radiation damage in monazite: Dr. Stefan Neumeier within "Conditioning" project; Dr. Guido Deissmann and Juliane Weber (IEK-6); external partners: Dr. Andre Filby, Dr. Ralf Kunz and Dr. Thomas Moeller (BRENK GmbH, Aachen), Prof. William J. Weber (University of Tennessee/ORNL, USA).

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Pyrochlore-type ceramics

- The study of thermophysical properties of pyrochlore-type solid solutions.

Thermal conductivity

- The thermal conductivities are derived from the calculated elastic parameters and Debye temperature, applying the Slack model.

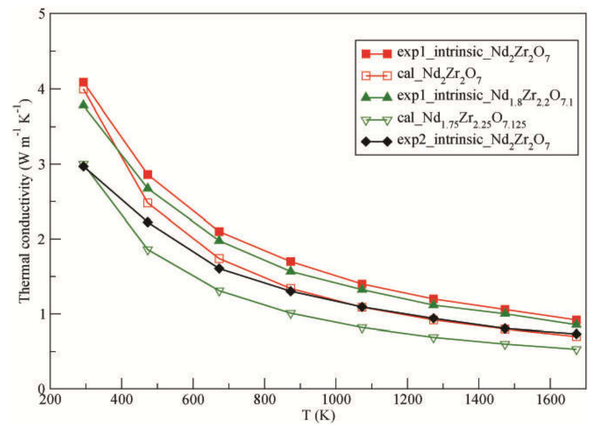


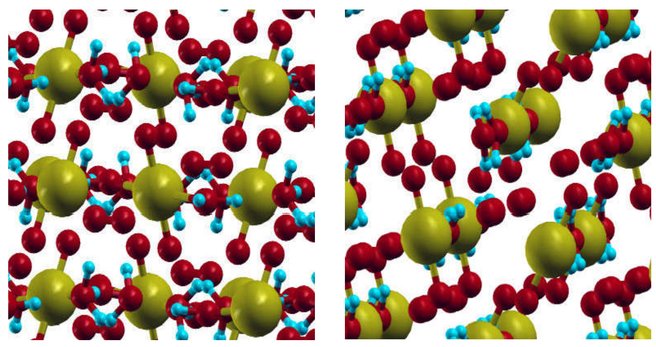
Fig. 7. The calculated and measured thermal conductivities of different $Nd_xZr_{1-x}O_{2-x/2}$ [6,7].

- The calculated thermal conductivities match reasonably the experimental data (intrinsic contribution) [6,7].

Metastudtite- and studtite-type ceramics

- Metastudtite (MST), and studtite (ST), are the two only known minerals containing peroxide. Metastudtite is the main natural peroxide mineral due to the irreversible dehydration of studtite. Both these phases may form in spent nuclear fuel exposed to water.

Np/Am incorporation



$(UO_2)O_2(H_2O)_4$ (ST) $(UO_2)O_2(H_2O)_2$ (MST)

Fig. 8. The configurations of ST and MST

- One of the interesting features of studtite is that it can incorporate radionuclides such as Sr and Cs as surface absorbed species, or Np as Np(V) or Np(VI).
- We computed Np and Am incorporation energies to check the possibility of incorporation of Am into ST and MST.

Table 1. The formation energy(eV) of Np/Am incorporation into ST and MST

	ST	ST (Np) [Am. Mineral 2010 95 (8-9)]	MST
Np/Am(III)	3.66/2.60		3.70/2.30
Np/Am(V)	1.50/2.86	1.12	1.75/2.48
Np/Am(VI)	1.09/2.20	0.42	1.05/2.18

- It is much easier to incorporate Np than Am into ST and MST, which is consistent with the experimental observation.

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