Atomistic simulations of novel nuclear waste forms: Cases of monazite and pyrochlore ceramics

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Large amount of highly radioactive waste is created worldwide mainly as a byproduct of electricity production [1]. Most of it is destined for long-term storage and eventual geological disposal. Because naturally occurring monazites and pyrochlores can contain significant amounts of radionuclides and preserve their crystalline structure for even billions of years, these materials are considered as potential matrix for permanent immobilization of minor actinides or Pu and for final waste disposal [2] [3]. We thus perform systematic *ab initio* investigation of various structutal and thermodynamic parameters of these ceramics [4] and deliver the information that is essential for assessment of stability of these materials under disposal conditions. We will discuss the computed excess enthalpies of mixing and the Margules interaction parameters that describe the non-ideality of the solid solutions of these materials with actinide and lanthanide cations. With atomistic simulations we were able to obtain relationships between the strength of the excess properties represented by the value of the Margules interaction parameters and the mismatch in the volumes of endmembers. We will discuss the results of these studies in context of stability of relevant waste forms. Because the high radiation damage resistance shown by selected pyrochlores ($A_2B_2O_7$) has a common basis with the disordering of cation and anion sublattices, and subsequent formation of defective fluorite, we calculated the cation antisite and anion Frenkel pair defects formation energies for a series of pyrochlores. Our results show that the anion Frenkel pair defect formation energy is negative in the compounds that tend to crystallize as a defective fluorite and positive for other pyrochlores. This correlation suggests that the low energy cost for defects accumulation is one of the main factors that lead to the order-disorder transition of selected pyrochlores and results in high radiation damage resistance of these ceramics.

[1] Ewing, (2015) *Nat. Mater.* **14**, 252. [2] Schlenz, et al., (2013) *Z. Kristallogr.* **228**, 113. [3] Lumpkin, (2001) *J. Nucl. Mater.* **289**, 136; [4] Li et al., (2014) *J. Solid State Chem.*, **220**, 137.