Ab initio modeling of excess mixing parameters of solid solutions relevant for nuclear waste management

PIOTR M. KOWALSKI*, YAN LI & VICTOR VINOGRAD

Institute of Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, Jülich, Germany, (*correspondence: p.kowalski@fz-juelich.de)

Nuclear waste as an unavoidable byproduct of nuclear technology requires adequate storing and disposal strategies. Disposal in deep geological formations is the most commonly considered waste management option. One approach is to immobilize the radionuclides in a ceramic waste form. Monazite, pyrochlore and zircon-type ceramics are of potential interest for actinides immobilization. Before these materials could be utilized as a matrix for nuclear waste disposal their thermodynamical properties must be well characterized. One of the parameters important for assessment of the stability of these materials in solid solutions with actinides is the excess enthalpy of mixing which in the case of simple solid solutions can be expressed by a simple polynomial containing adjustable parameters known as Margules interaction parameters. These parameters are usually difficult to measure accurately but can be estimated by *ab initio* method. We present our computational studies of monazite, pyrochlore and zircon-type solid solutions. We will demonstrate that the computational approach has to be carefully chosen to obtain reliable description of f-elements, which is crucial for correct derivation of the thermodynamic parameters, such as excess enthalpies of mixing or heat capacities of f-materials [1-3]. In particular we will demonstrate the importance of proper accounting for the strong electronic correlations (by DFT+U method). We will discuss the obtained excess properties of the considered solid solutions and the dependence of the interaction parameter on the endmembers volume mismatch. We will show that in case of monazite-type ceramics, the double substitution solid solutions, where two Ln^{3+} cations are replaced by one M^{2+} (e.g. Ca or Mg) and one An^{4+}, show much larger non-ideal effects than $(Ln^{3+},(An^{3+},Ln^{3+}))$ solid solutions. The follow up experimental studies aimed into validation of these results will also be discussed.

[1] Beridze & Kowalski (2014), *J. Phys. Chem. A*, **118**, 11797
[2] Blanca-Romero et al. (2014), *J. Comput. Chem.* **35**, 1339
[3] Li et al. (2014), *J. Solid State Chem.* **220**, 137