

Computational science in nuclear waste management: *ab initio* investigation of f-elements bearing Monazite.

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A safe disposal of nuclear waste is of great importance not only for the nuclear engineering but also for the general safety of society. One of the challenges in nuclear waste storage is to find suitable materials that are able to immobilize minor actinides such as Np, Am and Cm. The monazite-type orthophosphates are known to be able to incorporate actinides into their structure and preserve their crystalline character. Because of its resistance to radiation damage and chemical durability monazite is a promising host matrix [1]. In our institute we perform systematic experimental and computational studies of monazite ceramics that aim into in-depth understanding of the properties of these materials and their behavior upon incorporation of actinides. In our research we extensively use first-principles calculations to complement the experimental effort. Combination of both approaches allows us to learn how to reliably compute “tricky” 4f and 5f materials using modern methods of computational quantum chemistry.

In this contribution we present a systematic first-principles studies of the structural, thermodynamic, electronic and vibrational properties of Monazite-type LnPO₄ ceramics (where Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy). The calculations were performed using Density Functional Theory (DFT) with different variations of the generalized gradient approximation as well as with the DFT+U approach to correct for the strong on-site Coulomb repulsion. We calculated the structural parameters, vibrational frequencies, and the enthalpies of formation as well as the excess enthalpies of solid solutions of these compounds. Our results are confronted with a variety of experimental data (structural data [2,3], solid formation and solution enthalpies [3,4], IR and Raman spectroscopies [3,5]) and previous DFT calculations [3]. We will show that such a comparison allows for a proper assessment of the computational methods, and a better constraint of Hubbard U parameter for DFT+U method.

[1] H. Schlenz, J. Heuser, A. Neumann *et al.* (2013) in press
[2] H. Schlenz and J. Heuser (2013) in press [3] J. R. Rustad (2012) *American Mineralogist* **97**, 791 [4] K. Popa, R. Konings, and T. Geisler (2007) *J. Chem. Thermodynamics* **39**, 236 [5] K. Ruschel *et al.* (2012) *Miner. Petrol* **105**, 41.

First-principles investigation of equilibrium iron isotope fractionation in oxide and sulfide minerals

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The equilibrium isotope fractionation factor between two phases, which is a key parameter for the interpretation of isotopic variations among natural samples, can be determined from their reduced partition function ratios, also called β -factors. In most cases, β -factors cannot be measured directly but they can be calculated from vibrational properties following various approaches. For solids with Mössbauer-sensitive elements like Fe, the β -factor can be determined either from Mössbauer spectroscopy by measuring the temperature dependence of the isomer shift [1], or from nuclear resonant inelastic X-ray scattering spectra (NRIXS) by measuring the partial density of states of the resonant atom or by using the moments of the raw NRIXS spectrum [2,3]. An alternative approach consists in determining the theoretical vibrational density of states of the solid using first-principles calculations [4].

In this presentation, the Fe β -factors of oxide and sulfide minerals (mainly hematite, goethite and pyrite) computed using first-principles methods based on density functional theory with or without the addition of a Hubbard U correction (DFT and DFT+ U) will be compared with the available Mössbauer- and NRIXS-derived data. While all three methods must give consistent results, discrepancies are observed in some cases. The possible sources of discrepancy will be discussed.

[1] Polyakov (1997) *GCA* **61**, 4213-4217. [2] Polyakov *et al.* (2005) *GCA* **69**, 5531-5536. [3] Dauphas *et al.* (2012) *GCA* **94**, 254-275. [4] Blanchard *et al.* (2009) *GCA* **73**, 6565-6578.