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ScienceDirect

Energy Procedia 127 (2017) 416–424

Energy Procedia

www.elsevier.com/locate/procedia

International Youth Nuclear Congress 2016, IYNC2016, 24-30 July 2016, Hangzhou, China

LARGE SCALE SIMULATION OF NUCLEAR WASTE MATERIALS

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Abstract

Computer-aided simulations are valuable research tools for investigation of the properties of nuclear materials at atomic scale. This is because in principle, comparing with the experimental techniques, any system could be computed, including the experimentally challenging radiotoxic materials, and the only limitation is the availability and performance of the supercomputing resources and the approximate character of computational methods. Here we present an overview of our research activities on atomistic simulations of materials related to nuclear waste management. We discuss various structural, chemical, energetic, thermodynamic and radiation damage resistance properties of phosphate-based ceramic waste forms and nuclear graphite. Emphasis is put on selecting a reliable computational methodology. Our atomistic modeling effort complements the relevant experimental studies. We demonstrate that the combined atomistic modeling and experimental studies result in superior characterization of the investigated nuclear materials.

Peer-review under responsibility of the organizing committee of IYNC2016

Keywords: Nuclear waste materials; Simulation;

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1. Introduction

Safe management of nuclear waste is an important issue and strategies to deal with this problem are discussed in nuclear technology utilizing countries [1]. One of the widely accepted approaches is the conditioning of the waste by, for instance, immobilization of radionuclides in ceramic waste forms [2], and final deep geological disposal. Designing a durable nuclear waste disposal form requires in-depth characterization and understanding of the target

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Peer-review under responsibility of the organizing committee of IYNC2016
10.1016/j.egypro.2017.08.108

materials, such as monazite-type ceramics [3]. The materials properties of interest include the chemical and thermodynamic stability, the radiation damage resistance, the dissolution behavior and the corrosion resistance. Because many of these materials properties cannot be easily measured, if at all, the reliable atomistic modeling represents an important research tool in this field [4].

Because of the tremendous increase in the availability of the computing power, that rises by a factor of at least 100 per decade [5], it is now possible to perform large scale simulations of properties of chemically and structurally complex materials using *ab initio* (up to a few hundred atoms) and the force-field methods of computational chemistry and materials science [6]. In the atomistic modeling group in the IEK-6 part of the Institute of Energy and Climate Research at Forschungszentrum Jülich (Research Centre Jülich) we perform large scale atomistic simulations of various properties of nuclear waste related materials, including ceramic waste forms such as monazite-, xenotime- or pyrochlore-type ceramics, spent nuclear fuel (UO_2-based) and irradiated graphite. The investigated problems include: a reliable and feasible computational methodology for strongly correlated *f*-electrons systems [7,8,9], the structural [7], the elastic [10] and the thermodynamic materials properties [10,11,12,13], the radiation damage resistance [14,15], the surface chemistry [14,16] and the diffusion and energetics of defect formation [16,17], to name but a few. Here we will discuss in details the results of selected research activities. These include investigation of: the reliable *ab initio* computational approaches, the properties of monazite- and xenotime-type ceramic waste forms and irradiated graphite. In particular, we report new results on the elastic properties and the thermal conductivity of xenotime-type (LnPO$_4$) phosphates. These studies represent a scientific basis for nuclear waste management and the discussed results have been published in various scientific journals as indicated through the text.

2. Method

2.1 Ab initio methods

Density functional theory (DFT) is currently the most commonly used *ab initio* method [6]. This is because of its feasibility and good scaling with the number of atoms comparing to other methods of computational quantum chemistry (such as the post Hartree-Fock methods like hybrid DFT functional, MP2 or CCSD(T)). However, because DFT uses approximations which originate from the homogeneous electron gas, it usually has problems when applied to computation of strongly correlated and localized *d*- and *f*- electrons-containing systems such as lanthanide and actinide-bearing materials that constitute nuclear waste. Among other shortcommings, it overestimates the reaction enthalpies (by as much as 100 kJ/mol) [18,8] and fails even on the qualitative level, predicting metallic state for simple wide band gap actinide-oxides insulators (UO_2, NpO_2 or PuO_2) [19]. We thus utilize the DFT+*U* method, which treats the electronic correlations with the Hubbard model. In this model the strength of the Coulomb on-site repulsion, which causes the electronic correlation on the strongly localized *d* and *f* orbitals, is represented by the so-called Hubbard *U* parameter, which value is usually guessed or sometimes estimated from the sparsely available experimental data. In order to make the method a parameter free approach we derive the Hubbard *U* parameter value using recently developed *ab initio* methods such as the linear response (or constrained local density approximation, cLDA) [20] or the constrained random phase approximation (cRPA) [21]. In our research we use Quantum-ESPRESSO [22], CPMD [23] and FLEUR DFT [24] codes. The core electrons are represented by the ultrasoft pseudopotentials [25] and the plane-waves energy cutoff is set to 50 Ryd. More details on the computational setup are provided in the relevant publications.

2.2 Force fields methods

Because *ab initio* simulations are currently limited to no more than a few hundred atoms, large scale atomistic simulations involving thousands or millions of atoms are performed using force field methods in which the inter-atomic interactions are represented by an applied force field that is usually designed to reproduce some experimentally measured or computed *ab initio* materials properties. In our studies we use simple Buckingham-type force fields which parameters are fitted so the force field reproduces the *ab initio* data computed with the methodology described in the previous section. To perform these simulations we use GULP [26] and LAMMPS [27] simulation packages. The details on the fitting procedure and force fields parameters are provided by Ji et al. [14].

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3. Results

3.1 Feasible and reliable ab initio methodology

Shamov et al. (2007) [18] showed that DFT highly overestimates (by ~100 kJ/mol) the enthalpies of reactions that involve various uranium-bearing molecules. In that aspect we thus tested the DFT+U method with the Hubbard U parameter derived *ab initio* by using the linear response method of Coccocioni & Gironcoli (2005) [20]. We named the method DFT+U_{LR} hereafter. By computing the Hubbard U parameter values we made the DFT+U method a parameter free approach, which is opposite to majority of DFT+U studies that use the U parameter value that allows for fitting certain measured parameters, such as for instance the band gaps or the lattice parameters. For uranium-bearing materials the Hubbard U parameter value of ~4.5 eV is applied, as this value was deducted from the X-ray spectroscopic measurements of UO_2 [28,8]. We derived the Hubard U parameter values for several simple molecular and solid *An*-bearing compounds and found that it depends highly on the oxidation state of *An* cation, being larger for *An* in higher oxidation state [8,9], which is illustrated in Fig. 1. The obtained error of the reaction enthalpies is also significantly reduced and similar to the one shown by more computationally intensive method of quantum chemistry such as hybrid functionals or CCSD(T) [18,8,9] (Fig. 1).

We also tested the performance of the DFT+U_{LR} method for monazite- and xenotime-type (*Ln*PO_4) ceramics. We obtained excellent match to the *Ln*-O bond lengths (Fig. 2) and good prediction of the formation enthalpies [7,9]. We also found that using the *f*-in-the-core approach in which the *f*-electrons are not computed explicitly but are modeled by a pseudopotential (i.e. they are included in the pseudopotential's core) improves description of the energies providing prediction at the level of DFT+U_{LR} method and being computationally very stable. Therefore, we also use the f-in-the-core method for the derivation of the energy driven materials properties

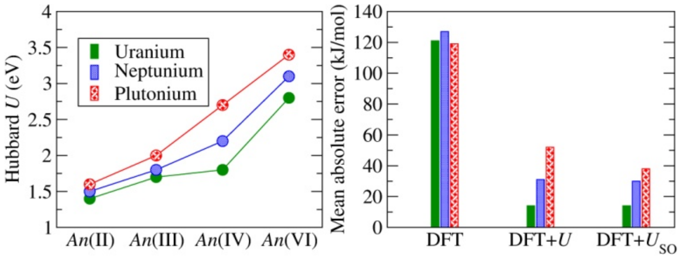

Fig.1. Left: The Hubbard U parameter as a function of *An* oxidation state [9,8], Right: The mean absolute error obtained by Beridze et al. [9] with different computational methods for the various *An*-molecules involving reactions including those considered by Shamov et al. (2007) [18].

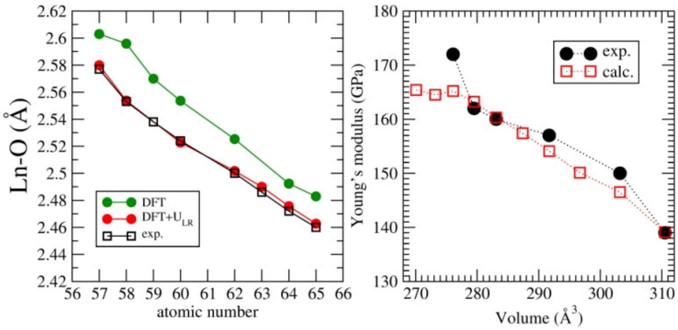

Fig. 2. The *Ln*-O bond lengths and the elastic moduli of monazite-type ceramics [7,10,13]

3.2 Thermodynamic and elastic properties of monazite- and xenotime-type ceramics

The computational methodologies outlined in Section 2 have been used in derivation of the various properties of monazite-type ceramics, including solid solutions. These include the excess enthalpies of mixing [10,11], the heat capacities [12] and the elastic properties [10]. These simulations allowed for derivation of the relationship between the volumes, the excess enthalpies of mixing, $H^E=Wx(1-x)$, where W is the Margules interaction parameter, and the elastic properties, namely Young's moduli *E*, and the solid solution endmembers volumes *V* and their difference *ΔV*, for monazite-type solid solutions [10]:

$$W = \frac{E}{6V}(\Delta V)^2$$

which is of great usage for the assessment of thermodynamic stability of radionuclide-bearing monazite-type ceramic waste forms, as it governs the formation of the miscibility gap [15]. This relationship allowed also the understanding of recently obtained thermochemistry data for the (Eu,La)PO_4 and (Gd,La)PO_4 solid solutions [29].

Here we computed the elastic parameters of selected xenotimes (Table 1 & 2) and the Margules interaction parameters for various relevant xenotime-type solid solutions (Table 3). The obtained Young's moduli are larger than the ones obtained for monazite (lighter lanthanides, Fig 2) and the value for $LuPO_4$ is slightly smaller than the one measured experimentally (202 GPa [30]). The Margules interaction parameters for the selected xenotime-type solid solutions are given in Table 4. In the calculations we applied the quasirandom structures-based computational approach that was used by Li et al. [11] for computation of monazite-type solid solutions. The direct *ab initio* calculations are consistent with the prediction of Eq. 1. We note that computed differences in volumes are overestimated [29] and when the experimental volumes are used instead, the Margules interaction parameter is slightly lower (Table 3).

Kowalski et al. [12] performed systematic calculations of the heat capacities of monazites. By considering the lattice vibrations and the thermal excitation of f electrons (Schootky contribution) they obtained excellent matches to the available experimental data. Recently, Kowalski et al. [13] demonstrated that these calculations can help in interpreting the low T heat capacity of $EuPO_4$ and (La,Eu)PO_4 solid solutions. Here, using the same computational methodology as Kowalski et al. [12], we computed the heat capacities of $LuPO_4$ xenotime. As shown in Fig. 3 we obtained perfect match to the experimental measurements [31,32], which validates further the computational approach used by Kowalski et al. [12].

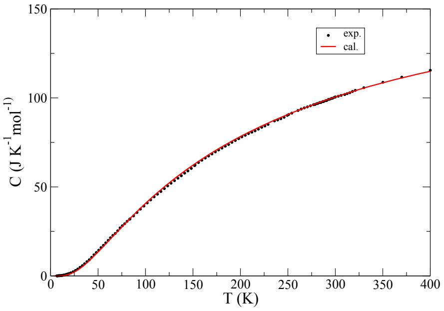

Fig.3. Heat capacities of $LuPO_4$ in the temperature range 0-400K. The solid line represents the computed values, the symbols show the experimental results [31,32].

The systematic computation of the phonon spectra and the elastic moduli of xenotime-type ceramics allow us for estimation of the thermal conductivity of these materials. To estimate the thermal conductivity we applied the Slack's model for the intrinsic lattice thermal conductivity κ [33], according to which

$$\kappa = A\frac{\bar{M}\delta\Theta_D^3}{\gamma^2 n^{2/3} T}$$

where M is the mean atomic mass, δ^3 is the average volume per atom, Θ_D is the Debye temperature, n is the number of atoms per primitive cell, T is temperature, γ is the high temperature limit of the acoustic phonon Grüneisen parameter, and *A* is a parameter related to γ, which can be calculated as follows [34]:

$$A = \frac{2.43\times10^{-8}}{1-0.514/\gamma-0.228/\gamma^2}$$

The acoustic phonon Grüneisen parameter is calculated as [35]:

$$\gamma = \frac{9(V_l^2 - \frac{4}{3}V_s^2)}{2(V_l^2 + 2V_s^2)}$$

where V_l and V_s are the longitudinal and transversal sound velocities computed from the elastic constants. The Debye temperature is computed as [36],

$$\Theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} V_m$$

where h is Planck's constant, k_B is the Boltzmann's constant, n is the number of atoms in the molecule, N_A is Avogadro's number, ρ is the density, M is the molecular weight and V_m is the average sound velocity, which is given by [35].

$$V_m = \left(\frac{3(V_l V_s)^3}{2V_l^3 + V_s^3}\right)^{1/3}$$

Table 1. The computed here Young's modulus E, bulk modulus B and shear modulus G of xenotime-type ceramics.

	B(GPa)	***G(GPa)***	***E(GPa)***
ErPO₄	154	68	177
YbPO₄	162	72	188
LuPO₄	168	75	194

Table 2. The computed here sound velocities of selected xenotime-type ceramics.

	V_s(m/s)	***V_l(m/s)***	***V_m(m/s)***
ErPO₄	3234	6266	3686
YbPO₄	3331	6296	3723
LuPO₄	3349	6345	3744

Table 3. The Margules interaction parameter W derived for xenotime-type solid solution using the following methods: the *ab initio* calculations (W_1), Eq. 1 with computed volumes (W_2) and Eq. 1 with the experimental volumes (W_3).

	W_1	***W_2***	***W_3***
(Tb, Lu)	***8.8***	***6.2***	***4.7***
(Er, Lu)	***2.1***	***1.6***	***1.0***
(Yb, Lu)	***0.31***	***0.24***	***0.11***
(Er, Yb)	***0.74***	***0.59***	***0.46***

Table 4. The parameters for calculating the thermal conductivity of xenotime-type ceramics

	γ	***δ(Å)***	***M(g)***	***Θ_D(K)***
ErPO₄	1.83	2.27	43.70	484
YbPO₄	1.81	2.25	44.67	493
LuPO₄	1.82	2.24	44.99	498

The selected parameters computed for considered xenotimes are reported in Table 2 & 4. As indicated in Table 5, by applying the outlined Slack's model we obtained a good match between the computed and the measured [33] values of the thermal conductivity.

Table 5. Thermal conductivity of xenotime-type ceramics in W/m/K. Experimental values are these of Hikichi et al. [33].

	Cal.	***Exp.***
$ErPO_4$	10.51	12.01
$YbPO_4$	11.58	11.71
$LuPO_4$	11.75	11.97

3.3 Radiation damage in monazite-type ceramics

Long-term ability to resist the radiation damage is a key property of a prospective, durable nuclear waste form. Consequently, we investigate the radiation damage processes in monazite-type ceramics. Our main aim has been to derive the threshold displacement energies, E_d, that are the minimum energies required to displace the atoms in the system. In these studies we applied force-fields-based molecular dynamics technique as described in Section 2.2. The values derived by Ji et al. [14] for the selected monazites are reported in Table 6.

Table 6. E_d values in eV derived for different monazite-type ceramics.

	$LaPO_4$	$GdPO_4$
Ln	56	51
P	75	72
O	8	8

Our results show that the E_d values do not depend much on the *Ln* cation. However, we found that because of the thermal motions, in monazite-type ceramics many initial dislocations easily recombine and the probability of defect formation depends strongly on the temperature [14]. These findings are similar to the ones obtained for $TiO_2(110)$ rutile [37], which is also a radiation damage resistant material. Ji et al. [14] also found a correlation between the E_d values and the energy barrier, $E_b=0.58E_d$, that separates the ground state from the defect states.

3.4 Surface chemistry of irradiated graphite

During operation of nuclear reactors significant amounts of ^{14}C containing irradiated graphite that requires disposal are produced. Safe nuclear graphite management strategies require understanding of the radiocarbon diffusion and its potential release mechanisms, which is driven by the surface chemistry. We thus perform ab initio atomistic simulation studies of the interaction of graphite surface with simple molecules (H_2O, CH_3,...). We found that water molecule is weakly bounded to the surface of ideal graphite (bonding energy of 0.037 eV), but easily undergoes dissociation on the defect sites, which is in line with the previous studies [38]. The adsorption on mono-vacancy and double-vacancy results in the absorption energies of 3.4 eV and 4.7 eV, respectively (Fig 4.). This could potentially explain hydrophilic character of irradiated graphite as opposite to the hydrophobic behavior of regular graphite

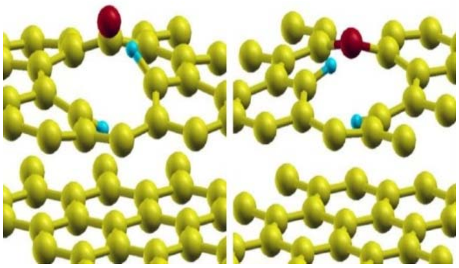

Fig. 4. Water adsorption configuration on graphite with mono- and double-vacancy [15].

3.5 Diffusion of ^{14}C in irradiated graphite

The self diffusion of ^{14}C in irradiated graphite is a key process to understand the mobility of radiocarbon in graphite-type nuclear waste. In Kowalski et al. [15] we have considered three main diffusion mechanisms: (M1) the diffusion through vacancy migration, (M2) the diffusion through direct interchange and (M3) the diffusion of interstitial atoms, as illustrated in Fig. 5. The obtained activation energies are 16.1 eV, 9.5 eV and 15.6 eV for the processes M1, M2 and M3, respectively, thus indicating that the direct interchange is the energetically preferable self-diffusion step. This is in line with the previous estimates performed considering C-C bond strengths by Dienes (1952) [39] who found 8.3 eV, 3.9 eV and 18.1 eV activation energies for the considered processes, respectively. We notice that all the predicted energies are substantially larger than the measured activation barrier for diffusion of 6.9 eV [40], although the modeling suggests that the direct interchange is the energetically most favorable process that leads to the self-diffusion of ^{14}C. Interestingly, we found that the large vacancy and interstitial formation energies, 7.6 eV and 7.4 eV, respectively, are the main contributors to the processes 1 and 2. The barriers for diffusion of a surface, interstitial atom and the vacancy are much smaller, 0.6 eV and 1.1 eV, respectively.

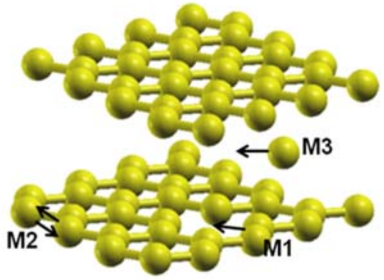

Fig. 5. The diffusion mechanism of ^{14}C. See text for explanation.

4. Conclusion

We discussed the atomistic modeling activities related to characterization of nuclear waste materials, including ceramic waste forms and nuclear graphite. The presented results on the structural, the thermodynamic, the chemical and the radiation damage resistance materials properties show the usefulness of the computer-aided atomistic simulations for characterization of experimentally challenging nuclear materials. We showed that properties, such as heat capacities, thermal conductivities or elastic moduli can be accurately modeled by carefully chosen *ab initio* approach. The successful applications and results were obtained mainly because of the selection of an appropriate computational approach. In that aspect we found the DFT+U_{LR} method as a good and computationally feasible tool which could be applied to reliable *ab initio* modeling of chemically complex *f*-elements bearing materials. We expect that in the incoming years, with the further increase in the available computing power and the performance of software, the atomistic modeling techniques will become very popular research tools in nuclear materials science.

Acknowledgements

Yaqi Ji is thankful to CSC China Scholarship Council for providing financial support for PhD studies in Germany at Forschungszentrum Jülich/RWTH Aachen. Funded by the Excellence Initiative of the German federal and state governments and the Jülich Aachen Research Alliance - High-Performance Computing. We thank the JARA-HPC awarding body for time on the RWTH and Forschungszentrum Jülich computing resources awarded through JARA-HPC Partition.

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