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Local structure in solid solutions of stabilised zirconia with actinide dioxides (UO_2, NpO_2)

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ABSTRACT

The local structure of $(Zr,Lu,U)O_{2-x}$ and $(Zr,Y,Np)O_{2-x}$ solid solutions has been investigated by extended X-ray absorption fine structure (EXAFS). Samples were prepared by mixing reactive $(Zr,Lu)O_{2-x}$ and $(Zr,Y)O_{2-x}$ precursor materials with the actinide oxide powders, respectively. Sintering at 1600 °C in Ar/H_2 yields a fluorite structure with U(IV) and Np(IV). As typical for stabilised zirconia the metal–oxygen and metal–metal distances are characteristic for the different metal ions. The bond lengths increase with actinide concentration, whereas highest adaptation to the bulk stabilised zirconia structure was observed for U–O and Np–O bonds. The Zr–O bond shows only a slight increase from 2.14 Å at 6 mol% actinide to 2.18 Å at infinite dilution in UO_2 and NpO_2. The short interatomic distance between Zr and the surrounding oxygen and metal atoms indicate a low relaxation of Zr with respect to the bulk structure, i.e. a strong Pauling behaviour.

1. Introduction

Cubic stabilised zirconia crystallises in a defect fluorite structure ($Fm\bar{3}m$), and forms solid solutions with actinide oxides. Due to its high thermal and radiation stability, stabilised zirconia is considered as a host matrix for plutonium and minor actinides (MA=Np, Am, Cm), either for their transmutation in dedicated reactor systems [1,2] or for conditioning in a radiation-resistant, durable form for final disposal [3,4]. In contrast, Zr and rare earth elements are important fission products and their progressive incorporation into the UO_2 lattice could alter the fuel properties during irradiation [5,6].

Information on the local atomic structure in such solid solutions assists in the understanding of mechanisms behind fuel or waste matrix properties and provides data for modelling their chemical and physical behaviour. Although X-ray diffraction reveals the lattice parameter of a solid solution, it is not suited to differentiate the local atomic structure of elements in the same crystallographic position. Such local structure information (bond lengths, coordination number, disorder) can be obtained from element specific methods such as extended X-ray absorption fine structure (EXAFS).

In principle, the bond length in an isovalent solid solution is limited by two cases, which reflect their ability to adapt to the bulk structure. Assuming that the atomic radii are approximately conserved (Pauling's concept), the individual bond length should be element specific and independent of the composition of the solid solution (i.e. no relaxation). In contrast, the virtual crystal approximation (VCA) could be valid and the bond lengths directly follow Vegard's law, similar to the lattice parameter (i.e. full relaxation) [7]. Early EXAFS investigations on both covalent and ionic systems [8] indicated that bond lengths follow an intermediate trend, i.e. they vary with the composition of the solid solution, but to a lower extend than expected by VCA. For example, such an intermediate behaviour is reported for the $(Th,U)O_2$ and $(Th,Pu)O_2$ solid solutions, where the relaxation is 32–35% for Th–O, but 47% and 54% for U–O and Pu–O, respectively [9,10]. In heterovalent solid solutions, like stabilised zirconia (YSZ), the bond lengths are also affected by the acceptance of vacancies and the associated reduction in the coordination number. The bond lengths in YSZ are element specific and nearly constant over a wide range of (Zr,Y) stoichiometries. [11,12]. EXAFS has been used to investigate the local structure of stabilised zirconia containing up to 20 mol% of actinides [13–16] and radiation effects in $Am_2Zr_2O_7$ [17,18]. Furthermore, EXAFS investigations covering a larger range in stoichiometry were performed on fluorite type solid solutions like $(U,Ce)O_2$ [19] and $(U,La)O_{2\pm x}$ [20].

The present work aims at the characterisation of the local structure of solid solutions containing stabilised zirconia and the actinide dioxides UO_2 and NpO_2 covering a wide stoichiometry

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range. Since $(Zr,Y)O_{2-x}$ is an envisaged matrix for nuclear application, $(Zr_{0.84}Y_{0.16})O_{1.92}$ and $(Zr_{0.5}Y_{0.5})_{1.75}$ were used to prepare $(Zr,Y,Np)O_{2-x}$ with two concentrations of oxygen vacancies. Unfortunately, the $(Zr,Y,U)O_{2-x}$ solid solution is not suited for conventional EXAFS investigations as the Y K (17,038 eV) and U L_3 (17,168 eV) edges are too close to derive structural information. Lutetium was selected to replace Y since it is invariably trivalent and does not form an ordered pyrochlore structure at $(Zr_{0.5}Lu_{0.5})O_{1.75}$.

2. Experimental

2.1. Sample preparation

$(Zr,Lu,U)O_{2-x}$ samples with Lu/Zr ratios of 0.2 and 1.0 were prepared by powder metallurgy using $(Zr,Lu)O_{2-x}$ precipitates calcined at 600 °C. The reactive stabilised zirconia precursor was mixed with U_3O_8 to obtain 6, 20, 50, 80, and 94 mol% U in $(Zr,Lu,U)O_{2-x}$. Pellets of the milled material were pressed and sintered at 1600 °C under Ar/H_2 atmosphere (24 h). After renewed milling, the material was pressed again and sintered under the same conditions. The $(Zr,Y,Np)O_{2-x}$ samples with 6, 20, 50, and 80 mol% Np were prepared in a similar manner starting from $(Zr,Y)O_{2-x}$ (Y/Zr=0.2 and 1.0) and NpO_2.

Powder X-ray diffraction patterns were obtained using a Bruker D8 diffractometer ($CuK\alpha_1$, Ge monochromator) equipped with a position sensitive detector (Vantec). Measurements were performed from 20 to 120° 2θ with incremental steps of 0.0085°. A single $Fm\bar{3}m$ phase was observed for all samples except $(Zr_{0.42}Lu_{0.08}U_{0.5})O_{1.96}$, where two cubic phases form. Attempts to prepare this compound by precipitation from a mixed Zr, Lu, U solution were also unsuccessful in obtaining a single phase.

2.2. EXAFS measurement

X-ray absorption spectra at the Zr, Y K-edge, and Lu, U and Np L_3-edge were recorded at the INE-Beamline [21] at the Ångströmquelle Karlsruhe, ANKA. The EXAFS oscillations were extracted according to standard procedures using WINXAS [22]. Spherical 8 Å clusters of atoms with the Cartesian coordinates of $(Zr,Lu,U)O_2$ and $(Zr,Y,Np)O_2$ were used for the calculation of the theoretical phase shifts, $\delta(k)$, and backscattering amplitude functions, $F(k)$, (FEFF8 [23]). The amplitude reduction factor was held constant at 1.0 for the EXAFS fits and the shift in threshold energy, ΔE_0, was varied as a global parameter. The EXAFS data were refined in R-space (1–4.5 Å) from the Fourier transformed k^3-weighted $\chi(k)$ data.

3. Results

The experimental EXAFS data for $(Zr_{0.67}Lu_{0.13}U_{0.20})O_{1.94}$ and $(Zr_{0.67}Y_{0.13}Np_{0.20})O_{1.94}$ are shown in Fig. 1 as an example. The k-range of the EXAFS data was limited by element absorption edges at next higher energies (e.g. Y K-edge EXAFS is limited by Np L_3-edge). The corresponding Fourier transforms (FT) reveals two peaks corresponding to approximately 8 oxygen and 12 metal (Zr+Lu+U or Zr+Y+Np) atoms, respectively. The experimental EXAFS data were fitted in R-space using fixed coordination numbers (N). The coordination number of the oxygen atoms was set to 8 for samples with Lu/Zr and Y/Zr=0.2. In case of the Lu/Zr and Y/Zr=1 samples N was set to values between 7 and 8, to account for the increase in oxygen vacancies with Y and Lu concentration.

Taking the different backscattering behaviour of Zr, Lu, U, and Np into consideration, the second FT peak was modelled with one or two metal backscatteres, depending on stoichiometry. For example,

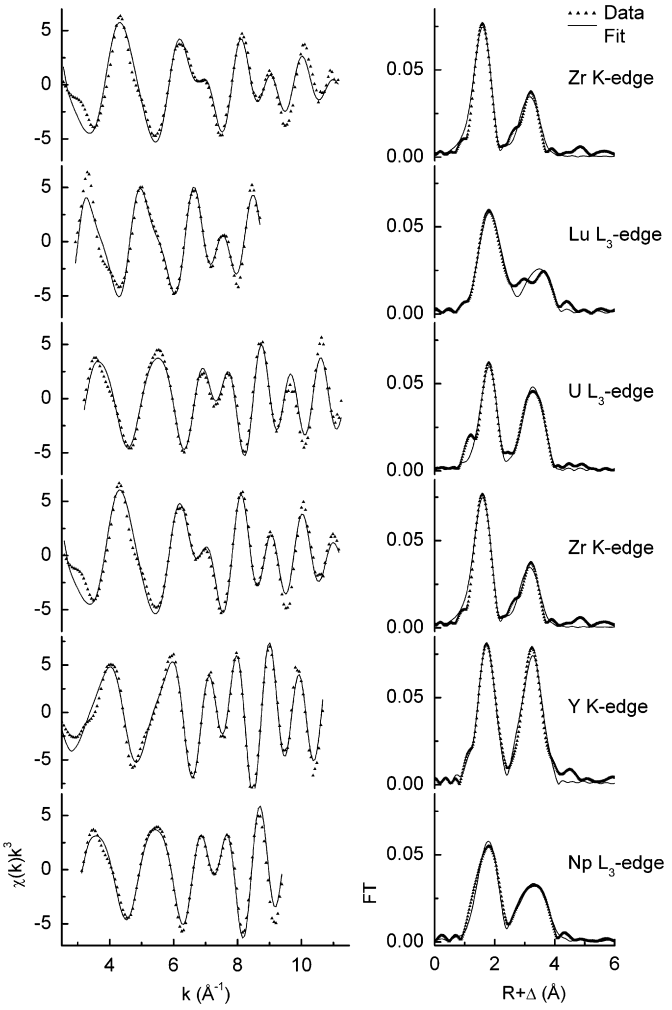

Fig. 1. k^3-weighted Zr, Y K-edge and Lu, U, Np L_3-edge EXAFS spectra of $(Zr_{0.67}Lu_{0.13}U_{0.20})O_{1.94}$ and $(Zr_{0.67}Y_{0.13}Np_{0.20})O_{1.94}$.

the second FT peak of samples with 94% actinide was modelled with 12 U atoms, as the Zr and Lu backscattering contribution is very low. To reduce the number of free parameters, Zr alone was chosen as backscatterer for Zr, Y and Lu (Lu/Zr=0.2 samples only) atoms in the second coordination shell. In addition, fits including all three metal atoms according to stoichiometry were tested, but the three metal–metal distances are too close to each other to derive meaningful structural parameters.

The Debye–Waller factor σ^2 for the two metal shells was correlated during the fit to minimise the strong correlation of the N, σ^2, and the backscattering amplitude of the different metal–metal paths. Because of the same reason an indepented refinement of metal coordination numbers and σ^2 was not performed and the obtained σ^2 values will not be discussed in the present paper.

A more distant coordination shell of 24 oxygen atoms at 4.3–4.5 Å ($R+\Delta$) had to be considered only for samples with high actinide content, as this coordination shell is strongly disordered in stabilised zirconia. The complete set of structural parameters is provided as Supplemental Data.

The derived metal–oxygen (M–O) bond distances are summarised in Figs. 2 and 3 for the $(Zr,Lu)O_{2-x}$–UO_2 and $(Zr,Y)O_{2-x}$–NpO_2 solid solutions, respectively. As is typical for stabilised zirconia compounds, the M–O lengths are element specific. The bond lengths in $(Zr_{0.79}Lu_{0.15}U_{0.06})O_{1.92}$ and $(Zr_{0.79}Y_{0.15}Np_{0.06})O_{1.92}$ are Zr–O 2.14 Å, Lu–O 2.27 Å, Np–O 2.27 Å, U–O 2.28 Å, and Y–O 2.31 Å. With increasing actinide content (i.e. lattice parameter)