Probing Covalency in the UO₃ Polymorphs by U M₄ edge HR-XANES

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Abstract. Local atomic and electronic structure investigations of uranium trioxide (UO₃) crystalline phases performed by the U M₄ edge HR-XANES technique is presented. The experimental U M₄ edge HR-XANES spectra of α-UO₃, β-UO₃ and γ-UO₃ polymorphic phases are compared with spectra of uranate (CaU₂O₇) and uranyl (UO₃•1-2(H₂O)) compounds. We describe a fingerprint approach valuable for characterization of variations of U-O axial bond lengths. Theoretical calculations of spectra using full-multiple-scattering theory (FEFF9.6 code) are performed. We have tested and selected input parameters, which provide best agreement between experimental and calculated spectra.

1. Introduction

Both structural and electronic properties of the uranium oxides are of fundamental and practical interest primarily due to the role of UO₂ in the nuclear fuel cycle [1, 2]. UO₂ is commonly exposed to oxidizing conditions and other binary oxides like for example UO₃ and U₃O₈ form at different stages of the nuclear fuel cycle [3]. UO₃ has the highest oxygen content among the uranium oxides. The chemical and physical properties of its polymorphs are also important to mining, milling, refinement and conversion processes that precede isotope enrichment within a nuclear fuel cycle [4]. X-ray absorption fine structure (XAFS) spectroscopy is successfully used for electronic and geometric structural investigations of uranium bearing materials [5]. The high energy resolution XAFS technique has gained popularity in the last years for structural investigations of broad range of materials [6]. The high energy resolution X-ray absorption near edge structure (HR-XANES) spectra at the U M₄ edge (3d₃/₂ → 5f) have spectral features with reduced broadening compared to the conventionally measured XANES [7-9]. Therefore this advanced technique provides relative energy positions of valence unoccupied actinide (An) f orbitals not accessible by the conventional XANES method [7-9]. In this study we discuss a fingerprint approach for detection of changes in the bond lengths between U and the two axial O atoms in uranyl type of bonding, i.e. U(VI) forms short (< 1.8 Å) covalent axial bonding with two O atoms (U-Oax). We present results of theoretical «ab-initio» full-multiple-scattering (FMS) HR-XANES calculations for the α-UO₃, β-UO₃ and γ-UO₃ phases by the FEFF 9.6 code [10].
2. Experiments and calculations

The α-UO₃ and β-UO₃ phases were synthesized as reported in [3]; γ-UO₃ is a commercial sample (Cameco Corp.); metaschoepite is prepared as reported in [11]. CaU₂O₇ was synthesized by recrystallizing UO₂•1-2(H₂O) in concentrated CaCl₂ aqueous solution. The structures of the studied compounds were confirmed by powder XRD measurements performed at the SUL-X beamline at ANKA (estimated purity > 95%). The obtained XRD patterns were compared with patterns from the PDF database (ICDD, [12]) using the DIFFRAC.EVA, Bruker software. Each compound with about 10 wt % of U was mixed with cellulose powder and pressed into a pellet. The U M₄ edge HR-XANES spectra of UO₂•1-2(H₂O), CaU₂O₇, α-UO₃, β-UO₃ and γ-UO₃ were measured using Johann type X-ray emission spectrometer recently installed at the INE-Beamline for actinide research at the ANKA synchrotron radiation facility, Karlsruhe; Germany [13,14]. The incident energy was monochromatized by a Si(111) double crystal monochromator (DCM). The sample, analyzer crystals and a silicon drift detector (KETEK) were arranged in a vertical Rowland geometry. The U HR-XANES spectra at the M₄ edge were obtained by recording the maximum intensity of the M₄ emission line (U M₄, 3337 eV) with five spherically bent Si(220) crystal analyzers with 1 m bending radius. The crystals were aligned at 75° Bragg angle. The DCM was calibrated by assigning 3725.5 eV eV to the maximum of the WL of a U M₄ edge HR-XANES spectrum of a UO₂ sample, which was repeatedly measured during the experiments.

The U M₄ HR-XANES spectra were calculated with the FEFF9.6 «ab-initio» quantum chemical code based on the full-multiple-scattering theory (FMS). The algorithm for the FMS method has been described elsewhere [15]. Phase shifts of the photoelectron were calculated in the framework of the self-consistent crystal muffin-tin (MT) potential scheme with 15% overlapping MT spheres. The spectra have been simulated using several types of exchange potentials: non-local, Dirac-Fock, Hedin-Lundquist or Dirac-Hara potentials. The best agreement with experiment has been achieved for the spectra calculated with the Hedin-Lundquist potential in Final State Rule (FSR) approximation for core-hole, reducing the 3d₃/2 core-hole life-time broadening (3.5 eV) to 2 eV and correcting the Fermi energy for UO₂•1-2(H₂O) and CaU₂O₇ by 0.5 eV. The atomic potentials were calculated self consistently for cluster sizes of about 7.0 Å around the absorber (including 101 atoms), while FMS calculations of U M₄ HR-XANES were performed for cluster of 10 Å radii (285 atoms). For the simulations of the HR-XANES spectra we have used the crystallographic data presented in Table 1.

Table 1. Crystallographic data used for calculations of the U M₄ HR-XANES spectra.

| Phase       | Space group  | Crystal system | Lattice parameters | #ICSD  |
|-------------|--------------|----------------|-------------------|--------|
| α-UO₃       | P-3m1 (#164) | Trigonal       | a=b=3.97 c=4.16   | 31628  |
| β-UO₃       | P121 1 (#4)  | Monoclinic     | a=3.91 b=14.33 c=10.34 | 14314  |
| γ-UO₃       | I41/amd (#141)| Tetragonal     | a=b=6.90 c=19.97  | 1093   |
| UO₂•1-2(H₂O)| Pbcn (#60)   | Orthorhombic   | a=14.68 b=14.02 c=16.71 | 31631  |
| CaU₂O₇      | R-3m (#166)  | Trigonal       | a=b=c=6.26        | 156714 |

3. Results and discussion

The U M₄ HR-XANES spectra of UO₃ polymorphs are compared with the spectra of UO₂•1-2(H₂O) and CaU₂O₇ (fig.1a). All U M₄ HR-XANES spectra have three distinct spectral features marked with A (~ 3727 eV), B (~ 3729 eV) and C (~ 3732 eV) in figure 1a. The A, B and C peaks have been assigned to electronic transitions of 3d₃/2 electrons to 5fδ/5fδ (A), 5fδ (B) and 5fδ(C) unoccupied valence orbitals of U(VI) in the form of UO₂²⁻ (uranyl) [8]. The hybridized U 5f and 6p orbitals form sigma
covalent bonds mainly with 2p orbitals of the Oax atoms therefore the energy position of peak C is essentially influenced by variations of the U-Oax bond length [9].

U forms uranyl and long > 1.8 Å (uranate) U-Oax bonds in metaschoepite (1.78 Å) and CaU$_2$O$_7$ (1.94 Å), respectively. These differences in bond lengths are reflected by the energy positions of peaks A, B and C. Peak A is shifted to higher energies (+ 0.2 eV), whereas peaks B (- 0.2 eV) and particularly C (- 1.1 eV) are shifted to lower energies for CaU$_2$O$_7$ compared to metaschoepite (UO$_3$•1-2(H$_2$O)). The elongation of the U-Oax in CaU$_2$O$_7$ leads to less electronic density in the vicinity of U, i.e. increased ionicity of the U-Oax bond [16]; as a result, due to worse screening of the core-hole, the main peak A is shifted to higher energies compare to this peak for the metaschoepite spectrum. The energy position of peak B can be in principle influenced by variations of the U-Oax but also by changes in bonding distances between U and the equatorial ligands.

Figure 1. U M$_4$ HR-XANES spectra of UO$_3$•1-2(H$_2$O), CaU$_2$O$_7$, α-UO$_3$, β-UO$_3$ and γ-UO$_3$ (a), experimental and calculated spectra for α-UO$_3$ (b), β-UO$_3$ (c) and γ-UO$_3$ (d) phases.

Up to several different U sites with variable U-Oax bond lengths are present in α-UO$_3$, β-UO$_3$ and γ-UO$_3$. α-UO$_3$ has two non-equivalent U positions; U forms bonds with the Oax atoms with two different average bond lengths, i.e. U(1)-Oax$_1$ = 2.08 Å and U(2)-Oax$_2$ = 2.39 Å. The uranium atoms in β-UO$_3$ can be divided into three groups: U(1) and U(2) have seven oxygen neighbors at distances varying between 1.69 Å and 2.72 Å, U(3) is coordinated by six oxygen atoms U(3)-Oax$_1$ = 1.79 Å, U(3)-Oax$_2$ = 2.17 Å which form a deformed octahedron, U(4) and U(5) have six oxygen neighbors and form uranyl type of bonding [17]. In γ-UO$_3$ all uranium atoms are surrounded by six oxygen atoms in distorted octahedral environment; the average U-Oax bond length is ≈ 1.78 Å [18]. The energy positions of features A, B and C are related to the average U-Oax distances for the three UO$_3$ compounds. The spectra of α- and γ-UO$_3$ are similar to the spectra of CaU$_2$O$_7$ and UO$_3$•1-2(H$_2$O),
respectively. Therefore we propose that in average the U-Oax bonds have more covalent character in γ-UO₃ compared to α-UO₃.

For each UO₃ phase the theoretical spectrum is a sum of weighted spectra obtained by placing the absorbing U atom at each non-equivalent crystallographic site. The FEFF9.6 code reproduces all spectral features at the correct energy positions for α-UO₃ and β-UO₃ (fig. 1b, c); some intensity differences are present. For γ-UO₃ (fig. 1d) the distances between features A and B (A-B), and B and C (B-C) are larger for the experimental (A-B ≈ 2 eV, B-C ≈ 3.5 eV) compared to the calculated (A-B ≈ 1.7 eV, B-C ≈ 2.2 eV) spectra.

4. Conclusions
We demonstrated that a fingerprint approach using U M₄ HR-XANES can be effectively applied for characterization of "uranyl" and "uranate" type of U-Oax bonding. Using this approach we showed that U-Oax bonds have likely more covalent character in γ-UO₃ compared to α-UO₃. The U M₄ HR-XANES spectra of the UO₃ polymorphs were performed within the full-multiple-scattering (FMS) formalism. We varied the input parameters to obtain best agreement between theory and experiment. The FEFF9.6 code emerges as an useful tool for calculation of U M₄ HR-XANES spectra, as it successfully reproduced all spectral features for some of the studied compounds.

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