Local structure and oxidation state of uranium in some ternary oxides:
X-ray absorption analysis

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Abstract

We investigated the local atomic and electronic structures of two related systematic sets of ternary uranium oxides, NaUO3–KUO3–RbUO3 and BaUO3–Ba2U2O7–BaUO4, by measuring the X-ray absorption near edge structure (XANES). The results are compared with calculations based on a self-consistent real space full multiple scattering analysis. We found a very good agreement between measured and calculated spectra, which indicates that the uranium ions are in a pure U5+ oxidation state in these compounds. The low energy shoulder observed in the U L3 edge XANES is an intrinsic feature of the uranium unoccupied 6d electronic states of the U5+ ions within the studied materials. Specific double shoulder features in the higher energy range of the U L5 edge XANES can be interpreted as indicative of the pure cubic perovskite structure.

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Keywords: X-ray absorption fine structure; Local and electronic structure; Uranium oxides

1. Introduction

In spite of the large amount of chemical, crystallographic and thermodynamic data available, the knowledge of the rather complicated uranium ternary oxides is still far from complete. One of the key topics is the local structure around the uranium ions and consequently their exact oxidation state in various compounds [1]. Difficulties with assigning valences in uranium compounds have been reported [2] for KUO3, RbUO3, NaUO3. Formally, these structures contain only one uranium valence, namely U5+. Their crystal structures are based on a perovskite structure with only one crystallographic position for U. As far as these two observations are concerned, there is no objection against classifying these materials as pure monovalent compounds. However, it has been reported that the XPS spectra of these uranates exhibit doublet structures for the U4f peaks [2,3], which can be interpreted as a signature of a mixed valence state.

X-ray absorption fine structure (XAFS) spectroscopy is a well-recognized method to study the local environment of actinides in their compounds [4]. XAFS is divided into two regions: Extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) [5]. The EXAFS data can be analyzed much easier, but contain only information on the radial distribution of atoms, while XANES analysis in principle allows one to define the full 3D local atomic geometry, including symmetry and fine details of the electronic structure of the materials under study. In order to extract the information from experimental X-ray absorption spectra, it is necessary to calculate these spectra using an advanced theoretical approach [6].

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For about two decades, XAFS spectroscopy was successfully used for the investigations of uranium bearing materials [7–17], including micro-XANES methods [18,19] and the study of oxygen XANES in uranium oxides [20,21]. Until now, the uranium XANES was mostly used without detailed theoretical analysis, as an empirical “finger-print” approach to study the most probable local structure around uranium ions (“uranyl” or “uranate” classification), or chemical shift analysis for the investigation of the uranium oxidation state.

In the present study the U L\textsubscript{3} edge XANES spectra have been measured in KUO\textsubscript{3}, RbUO\textsubscript{3}, NaUO\textsubscript{3}, BaUO\textsubscript{3}, Ba\textsubscript{2}U\textsubscript{2}O\textsubscript{7} and BaUO\textsubscript{4} and theoretical self-consistent field (SCF) full multiple scattering (FMS) simulations of XANES spectra have been performed for the analysis of the local atomic and electronic structure in these materials.

2. Experiment and computational method

The sample preparation method used for synthesizing the \(\text{AUO}_3\) powders with \(A = \text{Na, K, Rb}\) is described elsewhere [22]. For the barium compounds, similar methods were used. Stoichiometric quantities of the starting materials, barium carbonate \(\text{BaCO}_3\) and uranium oxide \(\text{U}_3\text{O}_8\) were intimately mixed using a mortar and pestle. For \(\text{BaUO}_4\), this mixture was treated in a box furnace at 900 °C in air. \(\text{BaUO}_4\) was reduced to \(\text{BaUO}_3\) at 1400 °C in a flow of dried \(\text{Ar/5\%H}_2\) (dew point <−50 °C). The preparation of \(\text{Ba}_2\text{U}_2\text{O}_7\), starting from \(\text{BaUO}_4\), requires accurate oxygen potential control, since this compound is only stable in a restricted oxygen potential domain [23]. This control can be achieved by mixing \(\text{Ar/5\%H}_2\) gas with \(\text{Ar/5000 ppm O}_2\) gas in the appropriate quantities to establish the correct \(\mu_{\text{O}_2}\) of −330 kJ/mol in the furnace at the treatment temperature of 1000 °C.

For the XAS measurements, a small quantity of each uranate (about 20 mg) was intimately mixed with boron nitride (BN), pressed into pellets and loaded in sealed, X-ray transparent containers. Uranium L\textsubscript{3}-edge X-ray absorption spectra were collected at the Rossendorf Beamline (ROBL) at bending-magnet port BM 20, of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The monochromator equipped with Si(111) double-crystal was used in channel-cut mode. Higher harmonics were rejected by two Pt-coated mirrors. The first mirror collimates the X-ray beam onto the monochromator crystal, the second mirror focuses the beam vertically to the sample. The vertical width of the secondary slit was 1.0 mm. Uranium L\textsubscript{III}-edge spectra were collected in transmission mode using argon-filled ionization chambers at ambient temperature and pressure. Data was collected in equidistant energy steps of 1.0 eV across the XANES region. Note that the energy resolution of the Si(111) crystal is about 3.5 eV at the U L\textsubscript{3}-edge. An Y metal foil (first inflection point at 17038 eV) was used for energy calibration.

Theoretical analysis of the U L\textsubscript{3} edges, was carried out on the basis of a SCF FMS method as it is implemented in FEFF8.4 code. The importance of the SCF approach to obtain a reasonable crystal potential for plutonium oxides and hydrides in XANES analysis has been shown before [24,25]. The algorithm for the FMS method has been described elsewhere [26]. 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 potential, Dirac-Fock potential, Hedin-Lundqvist potential and Dirac-Hara potential. Dependence of spectra on a relaxation of electrons in the presence of a core-hole has been studied as well. The best agreement with experiment has been achieved for the spectra calculated with the Hedin-Lundqvist potential in the presence of a core-hole. For the experimental energy resolution, a value of 2.0 eV was used. These factors were treated as contributions to the imaginary part of the self-energy term. Self-consistent potentials and corresponding phase-shifts were calculated for clusters of atoms having 5.0 Å radii, while FMS calculations of the U L\textsubscript{3} XANES were performed for atomic clusters of 8.0 Å radii.

For XANES spectra simulations, we have used the following crystallographic data: KUO\textsubscript{3}—\(\text{Pm3-m}\) (#221 space group) perfect perovskite structure with lattice parameter \(a = b = c = 4.293\ \text{Å}\) [22]; RbUO\textsubscript{3}—\(\text{Pm3-m}\) (#221 space group) perfect perovskite structure with lattice parameter \(a = b = c = 4.322\ \text{Å}\) [22]; NaUO\textsubscript{3}—\(\text{Pbnm}\) (#62 space group) orthorhombic structure with lattice parameters \(a = 5.7739\ \text{Å}, b = 5.9051\ \text{Å}, c = 8.2784\ \text{Å}\) [22]; BaUO\textsubscript{4}—\(\text{Pbcm}\) (#57 space group) orthorhombic structure with lattice parameters \(a = 5.744\ \text{Å}, b = 8.136\ \text{Å}, c = 8.237\ \text{Å}\) [27]. For BaUO\textsubscript{2} two possible structures have been tested, namely the ideal cubic perovskite group #221(\text{Pm-3m}) with \(a = b = c = 4.4074\ \text{Å}\) [28], and the orthorhombic \(\text{Pmmn}\) (#62 space group) structure with the following lattice parameters \(a = 6.2094\ \text{Å}, b = 8.7987\ \text{Å}, c = 6.2370\ \text{Å}\) [29]. For Ba\textsubscript{2}U\textsubscript{2}O\textsubscript{7}, the crystal structure reported in [23] was considered incorrect because of an unphysical O–O distance. The structure of this compound was refined on the basis of new X-ray diffraction data and the resulting structure was described in space group \(\text{Imma}\) (#74 space group) with \(a = 8.161\ \text{Å}, b = 11.317\ \text{Å}, c = 8.185\ \text{Å}\) [S. Van den Berge, to be published].

3. Results and discussion

In Fig. 1a, comparison between experimental and theoretical U L\textsubscript{3} edge XANES of KUO\textsubscript{3} and RbUO\textsubscript{3} crystals is presented. Since these materials have very similar crystal lattices and the same oxidation state of the uranium ions (U\textsuperscript{5+}), the XANES spectra look very similar: the lowest energy structure is the peak A with a low energy shoulder A\textsubscript{1}, which is found to be a characteristic feature for all U\textsuperscript{5+} compounds in the present study. In the higher
energy region of the XANES, we observed the shoulders B and C, which in our interpretation originate from the perfect perovskite structure (#221 space group) of the ternary uranium. From the relative energy shift of the C shoulder, it is easy to conclude that the U–O interatomic distances must be larger in RbUO₃ than in KUO₃. According to Natoli’s rule [5], \( R^2 \cdot \Delta E = \text{constant} \), where \( R \) are the interatomic distances between nearest neighbors and \( \Delta E \) is the energy separation between characteristic peaks of XANES. This rule applies well for uranyl ions complexed with organic acids [30]. Analysis of the U–O interatomic distances for KUO₃ and RbUO₃ is presented in Table 1 and indicates that the XANES method is sensitive enough to probe changes in the interatomic distances as small as 0.02 Å. Fig. 1 also demonstrates that the present SCF FMS approach reproduces all features of the U \( L_3 \) edge XANES in both KUO₃ and RbUO₃, including small energy shifts of the C peak, and the changes in the peak intensities. Thus, the theoretical framework was found to be quite adequate for detailed analysis of the U \( L_3 \) edge XANES in ternary uranium oxides.

As one can see in Fig. 2, where we present a comparison between the experimental and theoretical U \( L_3 \) edge XANES spectra of KUO₃ and NaUO₃, all changes can be reproduced by our theoretical model. We already mentioned that substitution of potassium by sodium in an \( AUO₃ \) crystal results in the distortion of the lattice with a corresponding transition from the perfect perovskite structure (#221 space group for KUO₃) to the orthorhombic structure (#62 space group for NaUO₃). One can find in Fig. 2 a clear evidence that the double B–C shoulder at the high energy region of the XANES spectrum (see Fig. 1), which is characteristic for the perfect cubic perovskite lattice of KUO₃ (as well as for RbUO₃), merged into a single shoulder B₁ at about 17,230 eV for the orthorhombic NaUO₃. Thus, one can use these “finger-print” shoulders in the high energy region of the U \( L_3 \) edge XANES to get an idea about the magnitude of the local distortions from the cubic symmetry in these ternary uranium oxides. At the same time, the main white lines for all three U⁵⁺ materials studied above (KUO₃, RbUO₃ and NaUO₃) have the same asymmetric structure with a low energy shoulder A₁. For the materials studied in the present work an analysis of the U d DOS calculated within \( L_3 \) core-hole potential shows that the low energy shoulder in U \( L_3 \) edge XANES is found to be a specific feature for U⁵⁺ compounds, but the absence of this shoulder on the U \( L_3 \) edge of BaUO₄ can be accidental and not specific for other U⁶⁺ oxides.

![Fig. 1. Comparison of the experimental U \( L_3 \) edge XANES in KUO₃ and RbUO₃ with the theoretical spectra.](image.png)

**Table 1**
Parameters of local structure around uranium ions and their states in the compounds under the study

<table>
<thead>
<tr>
<th>Compound</th>
<th>U oxidation</th>
<th>Symmetry group number</th>
<th>Number of O atoms around U</th>
<th>U–O distances used for simulations (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KaUO₃</td>
<td>U⁵⁺</td>
<td>221</td>
<td>6</td>
<td>2.146</td>
</tr>
<tr>
<td>RbUO₃</td>
<td>U⁵⁺</td>
<td>221</td>
<td>6</td>
<td>2.161</td>
</tr>
<tr>
<td>NaUO₃</td>
<td>U⁵⁺</td>
<td>62</td>
<td>2</td>
<td>2.142</td>
</tr>
<tr>
<td>BaUO₃</td>
<td>U⁴⁺</td>
<td>62</td>
<td>4</td>
<td>2.151</td>
</tr>
<tr>
<td>BaUO₄</td>
<td>U⁶⁺</td>
<td>57</td>
<td>2</td>
<td>2.191</td>
</tr>
<tr>
<td>Ba₂U₂O₇₇</td>
<td>U⁵⁺</td>
<td>74</td>
<td>2( U₁)</td>
<td>1.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2( U₂)</td>
<td>2.19–2.22</td>
</tr>
</tbody>
</table>

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Let us now consider BaUO₃. This compound is known to readily deviate from stoichiometry and as such, different structures have been reported. In [29], a compound with Ba₀.₉₈UO₃ stoichiometry has been described in the orthorhombic space group #62. Later, a perfect cubic perovskite structure has been proposed for BaUO₃₀.₀₂₃ [28], but it was finally reported that the attempts to prepare fully stoichiometric BaUO₃ were not successful and that the obtained material (BaUO₃₀.₀₅) must be refined as having the orthorhombic #62 symmetry group [31]. For the powder prepared in the framework of this study, a slight over-stoichiometry can be expected due to oxidation in air. Thus, we performed the simulation of the U L₃ edge XANES for BaUO₃ assuming two possible crystal lattice symmetries. In Fig. 3 we show a comparison between the experimental U L₃ edge XANES in BaUO₃ and theoretical spectra calculated for both cubic (#221 space group) and orthorhombic (#62 space group) crystal lattices. As one can see, the experimental spectrum agrees better with the theoretical one by assuming the orthorhombic symmetry. Therefore, the BaUO₃ sample used in the present study has, most likely, orthorhombic symmetry (group #62). This was confirmed by subsequent electron diffraction experiments in a Transmission Electron Microscope, where the deviation from cubic symmetry was clearly established. It is anticipated that tilting of the UO₆ octahedra occurs, and for symmetry Pnma, the expected tilting scheme is (a−b+a−). This results in unit cell dimensions of $\sqrt{2}a \times 2a \times \sqrt{2}a$ with $a$ the pseudocubic unit cell parameter. Although deviation from cubic symmetry was clearly evidenced, the electron diffraction experiments failed to identify unit cell multiplication and a tilting scheme could not be determined. A further study by neutron diffraction might enable the determination of the tilting scheme by refining the oxygen atom positions which are mostly affected by the expected tilting of the UO₆ octahedra.

Ba₂U₂O₇ has a structure which is more complex than the cubic perovskites, with two inequivalent positions of uranium ions (one can see nearest neighborhood around these two sites in Fig. 4). We refer to these two positions as U₁ and U₂ in Fig. 5 and in the following discussion. In Fig. 5, we present a comparison of the experimental U L₃ edge XANES in Ba₂U₂O₇ with the theoretical spectra calculated for two structural models. Initially we have...
considered the structure published in Ref. [23], but the shape of the theoretical XANES have been found to differ significantly from the experimental data. As one can see in Fig. 4 the shapes of XANES calculated for both U1 and U2 types of uranium atoms differ from the experimental spectrum, as well as the total theoretical spectrum. Therefore, we have performed a refinement based on the X-ray diffraction data for Ba2U2O7 (see Table 2). Although neutron diffraction data are required for a more accurately study of the positions of the oxygen atoms, the new refinement provides very satisfying results. Although the refinement was performed unbiased, the uranium local environments are now very similar (as can also be seen from the theoretical calculations of the XANES components). With these new structural parameters, the theoretical XANES spectrum at the U L3 edge agrees well with the experimental data. Small variations in the environments of the U1 and U2 ions (one can find numerical parameters in Table 1) result in variations of the partial XANES shapes, showing the sensitivity of XANES spectroscopy to small changes in local structure around the specific atomic site and also increasing the confidence in the correctness of the refined structure.

To study the effect of changes in the uranium oxidation state on the shape of U L3 edge XANES, we present in Fig. 6 a comparison of the experimental and theoretical U L3 edge XANES in two isoostructural materials—BaU4+O3, NaU5+O3 that have uranium ions in different oxidation states. It must be stressed that, in order to get a clear understanding of the influence of the oxidation state of the ion, one preferably needs to analyze the XANES of isostructural materials, or materials with very similar crystal structures. Accordingly, we used NaUO3, rather than Ba2U2O7 for this comparison. Alternatively, the modifications of the XANES shape that originate from the differences in the crystal symmetries can affect significantly the energy position of the inflection point of
the main rising edge of XANES (this point is generally used in the study of the chemical shifts in XANES analysis). As one can see in Fig. 6, when the oxidation state of the uranium ion changes from U⁵⁺ (NaUO₃) to U⁴⁺ (BaUO₃), the shape of the main white line of the U L₃ edge changes significantly (namely the low energy shoulder A₁ disappears and the white line becomes a symmetric one). On the other hand, the high-energy shoulder B₁ has the same shape for both materials, but is significantly shifted to higher energies in the case of NaUO₃. Using the semi-empirical rule mentioned above one can conclude that the U–O distance must be much smaller in NaUO₃ than in BaUO₃, which is in agreement with experiment (see Table 1).

As in all previous cases we find a very good agreement between experimental and theoretical XANES for BaUO₃.

To study the applicability of the chemical shift analysis for the determination of the oxidation state of uranium in ternary oxides, we have compared in Fig. 7 the renormalized (to have the same intensity as the main peak A) experimental U L₃ edge XANES in BaUO₃, NaUO₃ and Ba₂U₂O₇. It is observed that the tailing of the low energy shoulder A₁ in the NaU⁵⁺O₃ results in shifting of the inflection point of its rising edge so significantly, that, for this case, one cannot use the standard method to analyze the oxidation state. Thus, in the present case it will be better to use the position of the main maximum A as a control point for the determination of the uranium ion oxidation state.

To show that the SCF FMS method reproduces well enough the XANES data for ternary uranium oxides having different oxidation states of uranium, we present in Fig. 8 a comparison of the experimental U L₃ edge XANES in BaUO₃, Ba₂U₂O₇ and BaUO₄ (normalized) with the corresponding theoretical spectra.

By analysis of the shape of the main white line, one can conclude that the asymmetry of the main white line of the U⁵⁺ ions in ternary oxides is a characteristic feature of this oxidation state that does not depend on the crystal structure. When the oxidation state changes to U⁴⁺ or U⁶⁺, the symmetry of the main peak of the white line is restored. Thus, in this respect, the XANES calculations and data do not support the assumption of mixed valence in these compounds.

In view of the previously observed X-ray dichroism near the U L₃ edge in rubidium uranyl nitrate [32], it would be interesting for future work to measure and analyze...
theoretically the polarized $U_{L3}$-edge in the compounds under study to obtain more specific information on the electronic structure of these materials.

4. Conclusions

The SCF FMS method was found to be an adequate tool for the analysis of the $U_{L3}$-edge XANES of ternary uranium oxides. The calculated XANES spectra of the investigated compounds correspond very well with the experimental results and reproduce all features related to the valence changes between BaUO$_4$, Ba$_2$U$_2$O$_7$ and BaUO$_3$, as well as the variation in crystal structure between the cubic perovskite KUO$_3$ and RbUO$_3$ and the distorted, orthorhombic NaUO$_3$. It could be concluded that the XANES theoretical and experimental results support the assumption that only U$^{5+}$ ions are present in NaUO$_3$, KUO$_3$ and RbUO$_3$, as well as in Ba$_2$U$_2$O$_7$.

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