Further insights into the chemistry of the Bi–U–O system

Karin Popa,*a Damien Prieur,a Dario Manara,a Mohamed Naji,a Jean François Vigier,a Philippe M. Martin,b Oliver Dieste Blanco,a Andreas C. Scheinost,c Tim Prüßmann,d Tonya Vitova,d Philippe E. Raison,a Joseph Somersa and Rudy J. M. Koningsa

Cubic fluorite-type phases have been reported in the UIVO2–Bi2O3 system for the entire compositional range, but an unusual non-linear variation of the lattice parameter with uranium substitution has been observed. In the current extensive investigation of the uranium(IV) oxide–bismuth(III) oxide system, this behaviour of the lattice parameter evolution with composition has been confirmed and its origin identified. Even under inert atmosphere at 800 °C, UIV oxidises to UV/UVI as a function of the substitution degree. Thus, using a combination of three methods (XRD, XANES and Raman) we have identified the formation of the BiUVO4 and Bi2UVIO6 compounds, within this series. Moreover, we present here the Rietveld refinement of BiUVO4 at room temperature and we report the thermal expansion of both BiUVO4 and Bi2UVIO6 compounds.

Introduction

The Bi–U–O ternary system came to our attention in the frame of the safety assessment of lead bismuth eutectic (LBE) cooled fast reactors. The LBE cooled fast reactors concept is one of the systems being developed in Europe within the European Sustainable Nuclear Industrial Initiative (ESNII) and is the coolant of choice for the MYRRHA reactor project in Belgium.1 Thus, the phase relations in the Pb–Bi–U–Pu–O system should be studied in detail, in order to identify possible phases that could be formed during inadvertent fuel (MOX) – coolant (LBE) interactions.2

Very few compounds have been identified in the Bi–U–O ternary system to date. Bismuth(III) monouranate, Bi2UO6, is the only compound well characterized from a crystallographic point of view and has been prepared by several high- and low-temperature procedures.3–7 It was reported to exist in two closely related crystalline modifications. The room temperature form, α-Bi2UO6 (space group C2)8 undergoes a phase transition above 600 °C into the β-form (P3 space group).8,9 For this compound, the heat capacity was measured and a number of thermodynamic functions have been reported recently.10 BiUVO4 has been prepared and reported to have a defect fluorite structure (Fm3m) at room temperature.11,12 The pentavalent oxidation state of uranium was deduced from the co-proportionation reaction between stoichiometric amounts of UO2, U3O8, and Bi2O3. Further magnetic susceptibility measurements indicated a paramagnetic behaviour,13 consistent with the pentavalent oxidation state of uranium. However, no Rietveld refinement has been published for this compound to date.

Cubic fluorite-type phases have been reported in the system UIVO2–Bi2O3 for the entire compositional range by Hund.14 The non-linear variation of the lattice parameters observed in this study was explained based on the fact that the substitution increases the amount of anionic vacancies with increasing Bi2O3 content. However, this explanation assumes that the uranium remains in oxidation state IV in the synthesised powders. Thus, we initiated a comprehensive study on the oxidation states in the Bi–U–O system, focused on both uranium and bismuth. We present here the solid state synthesis of different compositions in the Bi–U–O system, the formation of the BiUVO4 and Bi2UVIO6 compounds in the reaction conditions, the Rietveld refinement of the BiUVO4 and the thermal expansion of BiUVO4 and Bi2UVIO6.

Materials and methods

Synthetic procedures

The uranium(IV) oxide–bismuth(III) oxide solid solutions were produced using the solid state reaction procedure previously reported (Hund).14 Thus, stoichiometric amounts of commer-
cial α-bismuth(III) oxide (Sigma-Aldrich, 99.999% trace metal basis) and UO₂₄₀ (COGEMA powder, stoichiometry calculated form the value of the lattice parameter) were reacted for 48 h at 800 °C under an argon atmosphere (with an oxygen content of 7 ppm) in specifically designed hermetically closed glove-boxes for handling radioactive materials. Note that the non-stoichiometric uranium oxide was chosen in this experiment in order to reproduce the working conditions presented by Hund. However, the composition having the ratio Bi:U = 1:1 and 2:1 were also produced starting from fully stoichiometric UO₂₀.85 under the same reaction conditions.

The α-Bi₂O₅ used for HT-XRD experiments was prepared by conventional solid state reaction (5 h of at 800 °C under air) of commercial α-bismuth(III) oxide with a stoichiometric amount of amorphous uranium(IV) oxide.

X-ray powder diffraction

α-Bi₂O₅ was characterised at room temperature by X-ray powder diffraction (XRD) using a Bruker D8 diffractometer mounted in a Bragg-Brentano configuration with a curved Ge (111) monochromator, a ceramic copper tube (40 kV, 40 mA) equipped with a LinxEye position sensitive detector. The data were collected by step scanning in the angle range 10° ≤ θ ≤ 120° at a 20 step size of 0.0092°. For the measurement, the powder was deposited on a silicon wafer to minimize the background and dispersed on the surface with several drops of isopropanol. The structural refinement was performed using the Fullprof2k suite. The shape of the peaks was described by a Pseudo-Voigt function and the background was fitted based on linear interpolation between a set of about 50 background points. The scattering factors of all elements were used.

The thermal expansion of BiUO₄ and α-Bi₂O₅ was followed by high-temperature X-ray diffraction experiments. The data were collected on a second Bruker D8 X-ray diffractometer mounted with a curved Ge (111) monochromator, a copper ceramic X-ray tube (40 kV, 40 mA), a LinxEye position sensitive detector and equipped with an Anton Paar HTK 2000 chamber. Measurements were conducted up to 600–700 °C under argon, in the angle range 10° ≤ θ ≤ 90° with a 20 step size of 0.017°.

HR-XANES spectroscopy

Uranium M₄-edge. The U M₄ (3728 eV) high energy resolution XANES (HR-XANES) spectra were recorded at the KIT INE-Beamline for actinide research at the ANKA synchrotron radiation facility (Karlsruhe, Germany) on 5 mg of powdered samples mixed with 20 mg of BN. The HR-XANES spectra have been collected using an Johann type multi-analyser X-ray emission spectrometer (MAC-Spectrometer). The incident X-ray beam was monochromatized by a Si(111) double crystal monochromator (DCM) and focused to 500 × 500 μm onto the sample. The MAC-Spectrometer comprised five spherically bent Si(220) analyser crystals with 1 m bending radius and a single diode silicon drift detector (KETEK VIRUS SDD). These two components and the sample were arranged in a vertical Rowland circle geometry and placed in a glove box filled with helium. Continuous helium flow has maintained a constant 0.1% O₂ content in the box during the experiments. The DCM was calibrated by setting 3724.5 eV to the maximum of the most intense absorption resonance (white line, WL) of a HR-XANES spectrum of a UO₂ reference compound. A short HR-XANES spectrum and a normal U M₄ (~3337 eV) emission lines of this reference were measured after each sample. Normal emission lines were also measured before the HR-XANES spectra for each sample in order to monitor the stability of the spectrometer. The U M₄ HR-XANES spectra were obtained by recording the intensity of the U M₄ emission line as a function of energy of the incident X-ray beam. The HR-XANES method is also often designated as high energy resolution fluorescence detected XANES (HERFD-XANES) or partial fluorescence yield XANES (PFY-XANES). The presented spectra have been normalized according to the maximum of the white line using the ATHENA software. This method provides unique qualitative informations about the oxidation states present in the systems. The spectra of (U⁰,V⁰)₂O₆ and (U⁰,V⁰)₂O₈ were collected earlier on the ID26 beamline of the ESRF synchrotron. The experimental energy resolution at the INE-Beamline and the ID26 beamline are about 1.3 eV and 0.9 eV, respectively. Bismuth and Uranium L₃-edge.

XANES data were recorded at the European Synchrotron Radiation Facility (ESRF, France). 5 mg of powdered sample was mixed with boron nitride (BN) and pressed into pellets for XANES measurements. The storage ring operating conditions were 6.0 GeV and 160–200 mA. The XANES spectra were recorded at room temperature in transmission mode at the ROBL beamline dedicated to actinide elements. A double crystal monochromator mounted with a Si (111) crystal was used. The energy calibration was achieved using platinum (Pt L₃ edge: 13 273 eV) and yttrium (Y K edge: 17 038 eV) foil lines of this reference were measured after each sample. For each XANES measurement, the spectra of the reference foil were systematically collected at the same time. Background subtraction and normalization have been achieved with ATHENA. To determine the oxidation states of bismuth, XANES spectra edges were compared to those of reference samples, i.e. Bi(II)₂O₅, Bi(III)₂O₅ and NaBiO₂-xH₂O, that were collected during the same experimental campaign. The oxidation state of uranium, was determined by comparing the absorption edges of the U L₃ XANES spectra to those of spectra of reference samples, i.e. UO₂, (U⁰,⁷⁰)₂O₈, (U⁰,⁷⁰)₂O₆, (U⁰,⁷⁰)₂O₄ and U⁰O₆. Oxidation states were derived using a linear combination fitting (LCF) of these normalized reference spectra.

Raman spectroscopy

Raman spectra were measured with a Jobin-Yvon® T64000 spectrometer used in the single spectrograph configuration. The excitation source was a Kr+ Coherent® continuous wave laser radiating at 647 nm, with a controllable nominal power, usually set to 100 mW at the exit of the cavity. The power impinging the sample surface was lower by approximately a factor 5. Spectra were measured in a confocal microscope with a 50-fold magnification and long focal distance (1 cm). This feature permits a good spectral resolution (±2 cm⁻¹) indepen-
dently of the surface shape, with a spatial resolution of 2 µm × 2 µm on the sample surface. The spectrophotograph angle was calibrated with the \( T_{2g} \) excitation of a silicon single crystal, set at 520.5 cm\(^{-1} \). The instrument is calibrated on a daily basis prior to measurement. Typical integration times ranged from 20 to 45 seconds with 3 cycles.

**Scanning electron microscopy**

A Philips XL40 Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectroscopy (EDS) was used. The sample grains were deposited on the usual carbon sticker and covered with Carbon to avoid charging. Each sample was observed at different magnifications and EDS analysis performed to confirm its homogeneity, comparing the elemental composition on the general view with those from smaller regions.

**Results and discussion**

**Elucidation of the non-linear behaviour of the lattice parameters in the uranium oxide–bismuth(III) oxide solid solution**

**Compositional characterisation.** The relative chemical composition of the obtained Bi–U–O samples, as determined by SEM-EDS, is: (1) Bi\(_{0.15}\)U\(_{0.85}\)O\(_{2.00}\); (2) Bi\(_{0.22}\)U\(_{0.75}\)O\(_{2.00}\); (3) Bi\(_{0.32}\)U\(_{0.68}\)O\(_{2.00}\); (4) Bi\(_{0.40}\)U\(_{0.60}\)O\(_{2.00}\); (5) Bi\(_{0.50}\)U\(_{0.50}\)O\(_{2.00}\); (6) Bi\(_{0.60}\)U\(_{0.40}\)O\(_{1.95}\); (7) Bi\(_{0.67}\)U\(_{0.33}\)O\(_{2.00}\); (8) Bi\(_{0.70}\)U\(_{0.21}\)O\(_{1.81}\); and (9) Bi\(_{0.85}\)U\(_{0.15}\)O\(_{1.70}\). The oxygen content was established based on the relative ionic metal composition (as determined by SEM-EDS) and their oxidation states (determined by XANES) as will be explained below (for the samples (1), (3), (5), (6), (7), and (8) – direct measurements, while for the samples (2), (4), and (9) – extrapolated).

**XRD study.** As already mentioned, cubic fluorite-type phases have been reported in the U\(_{IV}\) system, U\(_{O2}\)–Bi\(_{2}O_3\), over the entire compositional range by Hund.\(^{14}\) A non-linear variation of the lattice parameter has been observed, which was explained by the increase of anionic vacancies with increasing Bi\(_2O_3\) content, assuming uranium remained at the oxidation state IV (Hund).\(^{14}\) In the current investigation of the Bi–U–O system, we have confirmed this specific variation of the lattice parameter with composition, as shown in Fig. 1 and Table 1, suggesting that similar phases as Hund have been obtained.\(^{14}\) It can be observed that the samples rich in uranium follow a quasilinear trend up to Bi : U = 1 : 1.

In almost all the compositions, syntheses lead to the formation of well crystalline Bi–U–O solid solutions with a fluorite structure (inset Fig. 1). As this structural description comes from diffraction data, it only describes an “average” of the atomic organisation on a long distance. Being a solid-solution of uranium and bismuth, there is a shared crystallographic position of the cations, \textit{i.e.} a random distribution of the two elements in space.

Only Bi\(_{0.85}\)U\(_{0.15}\)O\(_{1.70}\) crystallises in a specific structure with a monoclinic space group. As illustrated in Fig. 2, the former structure is strongly fluorite related. For this reason, despite

---

**Table 1** Lattice parameters for the Bi–U–O compositions

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>( a, ) Å</th>
<th>( b, ) Å</th>
<th>( c, ) Å</th>
<th>( \beta, ^\circ )</th>
<th>( V, ) Å(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(<em>{0.15})U(</em>{0.85})O(_{2.00})</td>
<td>5.463 (1)</td>
<td>163.04 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.22})U(</em>{0.75})O(_{2.00})</td>
<td>5.465 (1)</td>
<td>163.22 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.32})U(</em>{0.68})O(_{2.00})</td>
<td>5.467 (1)</td>
<td>163.40 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.40})U(</em>{0.60})O(_{2.00})</td>
<td>5.472 (1)</td>
<td>163.85 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.50})U(</em>{0.50})O(_{2.00})</td>
<td>5.478 (1)</td>
<td>164.35 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.60})U(</em>{0.40})O(_{1.95})</td>
<td>5.516 (1)</td>
<td>167.83 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.67})U(</em>{0.33})O(_{2.00})</td>
<td>6.889 (3)</td>
<td>4.007(4)</td>
<td>9.691 (5)</td>
<td>90.13 (3)</td>
<td>266.96 (5)</td>
</tr>
<tr>
<td>Bi(<em>{0.70})U(</em>{0.21})O(_{1.81})</td>
<td>5.638 (1)</td>
<td>179.21 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(<em>{0.85})U(</em>{0.15})O(_{1.70})</td>
<td>5.612 (1)</td>
<td>176.75 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The O/M ratios have been derived from the U molar fractions and XANES measurements.

---

![Fig. 1](image1.png) Lattice parameter variation in the Bi–U–O system as a function of the substitution degree. For Bi\(_{0.67}\)U\(_{0.33}\)O\(_{2.00}\) (●), see discussions. Inset: XRD patterns of the different mixed oxides analysed in this study.

![Fig. 2](image2.png) Rietveld refinement of the sample Bi\(_{0.67}\)U\(_{0.33}\)O\(_{2.00}\) using a monoclinic cell (S.G. C\(_2\)) and a cubic one (S.G. Fm\(_{3m}\)). Despite a better description of the structure in the monoclinic space group, this second refinement highlights that the structure is fluorite related.
the poor quality of the refinement in Fm3m space group, the deduced lattice parameter obtained with this approach has been introduced in Fig. 1 for comparison with other compositions. Nevertheless, the monoclinic structure obtained for this composition (S.G. C2, α = 6.889(3) Å, β = 4.007(4) Å, γ = 9.691(5) Å, β = 90.13(3)°) strongly suggest the formation of the UVI compound α-Bi2UO6.5–10. This hypothesis is at first quite surprising, having in mind the synthesis method (reaction of stoichiometric amounts of commercial α-Bi2O3 oxide and UO2.10 at 800 °C under argon atmosphere). However, the oxidation state VI of uranium has been confirmed with XANES, as it will be presented in the next part. The source of the uranium oxidation are likely small amounts of molecular oxygen contained in the argon atmosphere.

**XANES measurements.** In order to investigate the oxidation states of uranium and bismuth, we performed an extensive Bi LIII and U LIII XANES and U MIV HR-XANES analysis for seven selected compositions. Unfortunately, the sample with the highest bismuth content could not be measured during the U MIV HR-XANES experimental campaign.

**Valence state of uranium.** The U MIV HR-XANES spectra of different Bi–U–O compositions are presented in Fig. 3 with those of the reference samples, i.e. UO2, (UV,UVI)3O8, (UV,UVI)3O8, (UV,UVI)3O8 and UO3. These spectra provide unique qualitative informations on the oxidation state in the systems. The uranium oxidation states and derived molar fractions from LIII XANES are provided in the Table 2. These results, together with those obtained from SEM-EDS analysis, were used to calculate the oxygen content within the different Bi–U–O compositions used during this study.

As previously reported19,20 herein we demonstrate that that the uranium oxidation states can be characterized using the U MIV edge HR-XANES technique. The HR-XANES spectrum of UO3 has a pronounced peak at 3724.5 (2) eV, due to the electronic transitions from the 3d5/2 core level to the unoccupied 5f states. The (UV,UVI)3O8 HR-XANES spectrum depicts a peak at the same energy position characteristic of UIV and also a peak at 3725.5 (2) eV which corresponds to UVI. The (UV,UVI)3O8 HR-XANES spectrum exhibits a white line at 3726.2 (2) eV attributed to UVI and a shoulder at the lower energy side with energy position characteristic for UVI. The energy positions of the white line of the UVI compound and the UVI peak in (UV,UVI)3O8 coincide (3726.2 (2) eV) and it is characteristic for UVI compounds.

Except for Bi0.79U0.21O1.81, the white lines of the Bi–U–O compositions shift toward higher energy with increasing the bismuth content. This suggests an overall oxidation of uranium over the compositional range. The XANES spectra of Bi0.11U0.85O2.00 and Bi0.12U0.68O2.00 exhibit the two features characteristics of UIV and UVI. However, it can be observed that the amplitude of the UVI peak decreases with increasing the bismuth content.

Regarding the Bi0.50U0.50O2.00 sample, its white line is a symmetric peak well aligned with the UVI peak of (UV,UVI)3O8. As would be expected from the electroneutrality rule, the least common factor (LCF) confirms that uranium is purely pentavalent for this composition. When increasing the bismuth content, the LCF shows that UVI is progressively formed in Bi0.60U0.40O1.95 and that a pure UVI compound is obtained on reaching Bi0.79U0.21O1.81. The formation of UVI is linked to a strong increase of lattice parameter. However, the white line of Bi0.79U0.21O1.81 shifts toward lower energy indicating the presence of UVI. This is in agreement with the lattice parameter decrease observed by XRD and Raman measurements.

**Valence state of bismuth.** XANES measurements at the Bi LIII have been performed to elucidate the bismuth valence state. The Fig. 4a and b present the Bi LIII XANES spectra of the Bi–U–O samples.

In the Bi LIII XANES spectra, there is a shift toward higher energies between the Bi0.33O2, Bi0.33O2 and NaBiO3·xH2O white lines passing from BiII to BiI. Although bismuth is trivalent in both Bi0.33O2 and Bi0.33O2, the XANES spectra are different and shifted from one another. This has already been reported21 for other isovalent compounds and can be understood from the difference of local environment. The NaBiO3·xH2O spectrum exhibits a pre-edge describing 2p1/2–6s transitions corresponding to pentavalent bismuth where the 6s levels are unoccupied. This feature is not observed in our compositions, indicating that Bi remains trivalent.

The white lines of the spectra of Bi0.50U0.50O2.00, Bi0.33U0.68O2.00, and Bi0.50U0.30O2.00 compositions have similar

---

**Table 2.** Uranium valence and molar fraction in the Bi–U–O compositions.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>UIV</th>
<th>UVI</th>
<th>UVI</th>
<th>RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi0.11U0.85O2.00</td>
<td>82</td>
<td>18</td>
<td>0</td>
<td>0.005</td>
</tr>
<tr>
<td>Bi0.12U0.68O2.00</td>
<td>44</td>
<td>56</td>
<td>0</td>
<td>0.020</td>
</tr>
<tr>
<td>Bi0.60U0.40O1.95</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>Bi0.60U0.40O1.95</td>
<td>0</td>
<td>74</td>
<td>26</td>
<td>0.002</td>
</tr>
<tr>
<td>Bi0.67U0.33O2.00</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0.006</td>
</tr>
<tr>
<td>Bi0.79U0.21O1.81</td>
<td>10</td>
<td>90</td>
<td>0</td>
<td>0.003</td>
</tr>
</tbody>
</table>

*The O/M ratios have been derived from the U molar fractions in respect of electroneutrality.*
energy positions of their absorption edges and overall shapes. This is an indicator that the local structure of these materials is very close. However, the white lines of the remaining samples are totally different and are shifted from one another, suggesting a different local environment for each composition.

Raman spectroscopy

The Raman spectra of the samples are shown in Fig. 5. Samples with high uranium content (up to a molar ratio Bi:U = 1:1) reflect very poorly, which explains the poor quality of their spectra (dashed black lines in Fig. 5). These spectra are compared with a spectrum from a polished surface of a pure commercial UO₂ pellet, shown in the thick bottom line in Fig. 5. Despite the noise, it can be seen that all these spectra are dominated by a band roughly centred at 445 cm⁻¹, which is assigned to the T₂g anti-symmetric U⁴⁺-O stretching vibration typical of eight-fold coordinated uranium in the fluorite structure. It has been observed many times in UO₂ and isomorphous compounds.³⁵⁻³⁰

Factor group theory indicates that it is the only Raman active mode in the Fm̅3m space group. As Bi³⁺ is dissolved in the UO₂ lattice, this band broadens and its peak position shifts towards slightly higher energy.

Nonetheless, the fact that the T₂g band dominates the spectrum indicates that a fluorite structure is maintained for Bi₀.15U₀.85O₂.00, Bi₀.32U₀.68O₂.00, Bi₀.50U₀.50O₂.00, and Bi₀.60U₀.40O₂.00 compositions. The broadening of the T₂g mode could arise from the local disorder caused by the Bi³⁺ cations in the fluorite structure. Close to the T₂g band, a few weak bands are observed around 570 cm⁻¹ and 630 cm⁻¹ which likely are linked to oxygen defects in the fluorite structure. Their presence reflects a breakdown of the translational symmetry and a reduction of the point group symmetry. Interestingly, their intensity is independent of the Bi³⁺ concentration, which could suggest that doping with Bi³⁺ has little effect on the oxygen sublattice and that charge compensation is then maintained by uranium atoms for compositions below Bi₀.50U₀.50O₂.00. The band at 630 cm⁻¹ increases for Bi₀.32U₀.68O₂.00 and Bi₀.40U₀.60O₂.00, which is similar to observations for U₄O₉. All of these observations are in agreement with the presence of mixed valence U⁴⁺/U⁵⁺ in the material and are consistent with XANES data.

At higher bismuth content, a different spectral form is observed (presented in green in Fig. 5), reflecting a complete change of the original fluorite local symmetry, though long range order probed by XRD indicates that a fluorite organisation remains for Bi₀.60U₀.40O₂.00, Bi₀.85U₀.15O₁.70, and Bi₀.85U₀.15O₁.70. These Raman spectra, of much better quality, are largely dominated by a strong band centred around 717 cm⁻¹. The increase in the number of Raman bands indicates a decrease of local symmetry. The band at 445 cm⁻¹ (T₂g) broadens with increasing the bismuth content together with
the appearance of weak features at low frequencies \( \sim 210 \text{ cm}^{-1} \) and \( 280 \text{ cm}^{-1} \) (typically for \( \text{Bi}_{0.60}\text{U}_{0.40}\text{O}_{1.95} \) and \( \text{Bi}_{0.67}\text{U}_{0.33}\text{O}_{2.00} \)). These modes (at \( 210 \text{ cm}^{-1} \) and \( 280 \text{ cm}^{-1} \)) are also present in the Raman spectrum of \( \text{Bi}_2\text{O}_3 \), correspond to the Van Hove singularities at the gamma point of the Brillouin zone and can be assigned to Bi–O stretching vibrations. The broadening of the 445 cm\(^{-1}\) band is a consequence of an increased frequency distribution of the U–O and Bi–O vibrations, very likely due to an increased local disorder in the short range. Therefore, the assignment of this band to pure oxygen motions in a monoclinic or cubic phase is not straightforward. The XRD results suggest that this local disorder is also present in the long range for \( \text{Bi}_{0.67}\text{U}_{0.33}\text{O}_{2.00} \), a monoclinic phase.

Despite the clear distortion at local range and by analogy with the Raman spectra of \( \text{U}_3\text{O}_8 \), \( \text{UO}_3 \), and \( \text{UO}_2^{2+} \) ion\(^{32,33} \), the peak around 717 cm\(^{-1}\) can be attributed to a Raman active U–O stretching vibration of \( \text{UO}_8 \) polyhedra with non-bonding oxygens, in close geometry to the \( \text{UO}_2^{2+} \) species. This assignment agrees well with the Raman spectrum of the hexavalent uranium compound \( \text{CaUO}_4 \), where this vibration was clearly identified as the \( \nu_1 \) stretching mode of the uranyl \( \text{UO}_2^{2+} \) ion.

Combining these observations with the XRD and XANES results, one can draw several conclusions. It can be observed, that the spectra of \( \text{Bi}_{0.32}\text{U}_{0.68}\text{O}_{2.00} \) and \( \text{Bi}_{0.50}\text{U}_{0.50}\text{O}_{2.00} \), displayed in Fig. 6, the \( T_{2g} \) band typical of the fluorite structure and oxygen defect bands between 570 and 630 cm\(^{-1} \).\(^{15} \) The latter lines are attributed to \( T_{1u} \) LO phonons Raman inactive in the absence of oxygen defects. They are not affected by \( \text{Bi}^{III} \) doping, suggesting that only the uranium(\( \text{IV} \)) atoms change to uranium(\( \text{V} \)) to compensate the electric charge on addition of \( \text{Bi}^{III} \). The \( T_{2g} \) band clearly dominates the spectrum of the uranium-rich samples suggesting that the fluoride structure is maintained, whereas, in the bismuth rich region two observations can be made: (i) the band at 445 cm\(^{-1}\) broadens and its intensity reduces significantly mainly due to the increase of the local disorder at the short range distances and (ii) the dominance of the U–O stretching mode at 717 cm\(^{-1}\) suggesting formation of \( \text{UO}_x \) species with non-bonding oxygens (similar to uranyl ions).

The spectrum of the pure \( \text{U}^{VI} \) phase \( \text{Bi}_{0.67}\text{U}_{0.33}\text{O}_{2.00} \) is even more strongly dominated by this latter line in agreement with the layer organisation of \( \alpha\)-\( \text{Bi}_2\text{UO}_6 \).

A special case of a \( \text{U}^{V} \) phase: \( \text{BiUO}_4 \)

At 50 mol\% of \( \text{UO}_2 \) and \( \text{Bi}_2\text{O}_3 \), a fluorite-type phase of general formula \( \text{U}_{0.5}\text{Bi}_{0.5}\text{O}_2 \) (or \( \text{BiUO}_4 \)) forms. The cell parameter 5.478 (1) \( \AA \), is larger than \( \text{UO}_2 \) (5.471 \( \AA \)). This is consistent with the average ionic radii of \( \text{Bi}^{III}_8 \text{CN} (1.17 \AA) \) and \( \text{U}^{IV}_8 \text{CN} (0.93 \AA) \), with the former being slightly larger than ionic radius of \( \text{U}^{IV}_8 \text{CN} = 1.00 \AA \). In \( \text{U}_{0.5}\text{Bi}_{0.5}\text{O}_2 \), the average distance M–O is 2.372 \( \AA \). The X-ray diffraction pattern with Rietveld refinement is shown in Fig. 7 and fitting results are provided in Tables 3 and 4. For oxygen atoms the displacement parameter \( B_{iso} \) is high, suggesting local disorder in agreement with the Raman observations.

The evolution of the unit-cell volume of \( \text{X}^{III}\text{UO}_4 \) phases as a function of eight-fold coordinated cationic radius (Fig. 8) would confirm that \( \text{BiUO}_4 \) belongs to this family. Note that \( \text{FeUO}_4 \) and \( \text{CrUO}_4 \) are not cubic.\(^{36} \) For some of these \( \text{X}^{III}\text{UO}_4 \) type compositions (\( \text{X}^{III} = \text{Bi}, \text{Sc}, \) and \( \text{Y} \)), the pentavalent oxidation state of uranium was proven based on magnetic susceptibility measurements.\(^{13,45} \) This might be an indication that all the other \( \text{X}^{III}\text{UO}_4 \) compositions shown in this graph are pure pentavalent uranium phases.
Thermal expansion of BiUO₄ and α-Bi₂UO₆

The relative variation of the cell parameters of BiUO₄ and α-Bi₂UO₆ with temperature is presented in Fig. 9. The transition temperature of α-Bi₂UO₆ (C2 space group) to β-Bi₂UO₆ (P3 space group) occurs between 600 and 800 °C, while the cubic BiUO₄ start to decompose into two phases above 700 °C. The expansion is more limited along the a and b directions compared to c, because of the edge-sharing of the UO₈ polyhedra (the thermal expansion along the c axis is more pronounced because of the layer structure of α-Bi₂UO₆).

Table 3 Unit cell parameters and results of the Rietveld refinement for BiUO₄

<table>
<thead>
<tr>
<th>Formula unit</th>
<th>a (Å)</th>
<th>V (Å³)</th>
<th>Space Group</th>
<th>Z</th>
<th>Rwp</th>
<th>Rp</th>
<th>Rb</th>
<th>Rexp</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiUO₄</td>
<td>5.478 (1)</td>
<td>164.35 Å³</td>
<td>Fm3m (N° 225)</td>
<td>4</td>
<td>7.76%</td>
<td>5.58%</td>
<td>2.08%</td>
<td>3.83%</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Table 4 Atomic positions in the BiUO₄ compound

<table>
<thead>
<tr>
<th>Atom</th>
<th>Oxidation state</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Biso (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>3⁺</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.38</td>
</tr>
<tr>
<td>U</td>
<td>5⁺</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.38</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Trivalent bismuth, which is seven-fold coordinated, is poorly bonded to oxygen.

The linear thermal expansion (LTE) is defined as

\[
\text{LTE}_{25°C}(T) = \left( \frac{\text{x}(T) - \text{x}(25°C)}{\text{x}(25°C)} \right)
\]

The polynomial interpolation of the experimental data are presented in Fig. 9 and gives for the cubic BiUO₄:

\[
\text{LTE}_{25°C}(T) = -3 \times 10^{-4} + 1.47 \times 10^{-5} T(°C) + 4.1 \times 10^{-9} T^2(°C)
\]

Similarly, the LTE for the different orientations in Bi₂UO₆ are:

a: \[
\text{LTE}_{25°C}(T) = -1 \times 10^{-4} + 3.2 \times 10^{-6} T(°C) + 8.8 \times 10^{-9} T^2(°C)
\]
b: \[
\text{LTE}_{25°C}(T) = 1 \times 10^{-4} - 2.0 \times 10^{-7} T(°C) + 8.2 \times 10^{-9} T^2(°C)
\]
c: \[
\text{LTE}_{25°C}(T) = -5 \times 10^{-4} + 1.65 \times 10^{-5} T(°C)
\]

Conclusions

The LBE cooled fast reactor concept is the basis of the MYRRHA reactor project in Belgium. As a part of the safety assessment for such reactors, detailed knowledge of potential lead and bismuth uranates/plutonates phases that could form in the event of a pin breach is needed. The present work completes our study performed in order to identify potential reaction products in the Bi–Pb–U–Pu–O system for the safety assessment for LBE cooled fast reactors.

In the current extensive investigation of the uranium(IV) oxide–bismuth(III) oxide system, the unusual behaviour of the lattice parameter variation with composition as observed by Hund14 has been confirmed and its origin identified in the oxidation state of uranium. Even under inert atmosphere at 800 °C, U⁴⁺ oxidises to U⁵⁺ as a function of the substitution degree. We have identified the formation of the BiUO₄ and Bi₂UO₆ compounds, within this series. All the compositions crystallise in a fluorite-related structure, but the actual symmetry of Bi₂UO₆ is monoclinic. Raman spectrometry indicates changes in the local symmetry from six-fold uranium coordination to an eight-fold coordination (deduced as a func-
tion of composition) which is not observable in the long range ordering (probed by XRD). EXAFS or neutron diffraction measurements are needed in order to give more details on the local structure in those compositions.

Acknowledgements

This work was performed in the frame of the “Safe exploitation related chemistry for HLM reactors (SEARCH)” Collaborative Project (Contract Number: 295736) in the Seventh Framework Programme of the European Commission. The authors acknowledge Daniel Bouexière and Giorgio Pagliosa for room- and high-temperature X-ray diffraction measurements. We authors acknowledge the ANKA and ESRF synchrotron facilities for provision of beam time. XAS measurements have been supported by the European FP7 TALISMAN project, under contract with the European Commission.

Notes and references

3 J. G. De Jong and Ph. A. Batist, Requeil, 1971, 90, 749–754.
Repository KITopen

Dies ist ein Postprint/begutachtetes Manuskript.

Empfohlene Zitierung:

Further insights into the chemistry of the Bi–U–O system
doi:10.5445/IR/1000055434

Zitierung der Originalveröffentlichung:

Further insights into the chemistry of the Bi–U–O system
doi:10.1039/C6DT00735J

Lizenzinformationen: KITopen-Lizenz