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

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Cubic fluorite-type phases have been reported in the UO2-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 oxides to 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 BiUO4 and Bi2U3O8 compounds, within this series. Moreover, we present here the Rietveld refinement of BiUO4 at room temperature and we report the thermal expansion of both BiUO4 and Bi2U3O8 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 out the systems being developed in Europe within the European Sustainable Nuclear Industrial Initiative (ESNII) and is the coolant of 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 (P-3 space group).8,9 For this compound, the heat capacity was measured and a number of thermodynamic functions have been reported recently.10

BiUO4 has been prepared and reported to have a defect fluorite structure (Fm-3m) at room temperature.11-12 The pentavalent oxidation state of uranium was deduced from the coproporportionation 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 UO2-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 BiUO4 and Bi2U3O8 compounds in the reaction conditions, the Rietveld refinement of the BiUO4 and the thermal expansion of Bi2UO4 and Bi2U3O8.

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 commercial α-bismuth(III) oxide (Sigma-Aldrich, 99.999% trace metal basis) and UO2 (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 gloveboxes for handling radioactive
materials. Note that the nonstoichiometric 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 UO$_2$ under the same reaction conditions.

The α-Bi$_2$UO$_4$ 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(VI) oxide.

**XRD diffraction**

α-Bi$_2$UO$_4$ 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 LinX Eye position sensitive detector. The data were collected by step scanning in the angle range 10° ≤ 2θ ≤ 120° at a 2θ step size of 0.0092°. For the measurement, the powder was deposited on a silicon wafer to maintain 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 BiUO$_4$ and α-Bi$_2$UO$_4$ 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 (1, 1, 1) monochromator, a copper ceramic X-ray tube (40 kV, 40 mA), a LinX Eye 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 16° ≤ 2θ ≤ 90° with a 2θ step size of 0.017°.

**HR-XANES spectroscopy**

**Uranium M$_{IV}$ edge**

The U M$_{IV}$ (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 x 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% O$_2$ 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 UO$_2$ reference compound. A short HR-XANES spectrum and a normal U M$_{IV}$ (~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 M$_{IV}$ HR-XANES spectra were obtained by recording the intensity of the U M$_{IV}$ 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 (U$^{VI}$,U$^{IV}$)$_2$O$_9$ and (U$^{VI}$,U$^{IV}$)$_3$O$_9$ 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 L$_{III}$ edge.

XANES data were recorded at the European Synchrotron Radiation Facility (ESRF, France). 5 mg of powdered sample were 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 L$_{III}$ edge: 13273 eV) and yttrium (Y K edge: 17038 eV) foil inserted between the second and third ionization chambers. 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$^{VI}$O$_9$, Bi$^{IV}$O$_6$, and NaBi$^{IV}$O$_3$·H$_2$O, that were collected during the same experimental campaign. The oxidation state of uranium, was determined by comparing the absorption edges of the U M$_{IV}$ XANES spectra to those of spectra of reference samples, i.e. U$^{VI}$O$_9$, (U$^{VI}$,U$^{IV}$)$_2$O$_9$, (U$^{VI}$,U$^{IV}$)$_3$O$_9$, and U$^{IV}$O$_6$. 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$^{-1}$) independently of the surface shape, with a spatial resolution of 2 μm x 2 μm on the sample surface. The spectrograph angle was calibrated with the T$_{2g}$ excitation of a silicon
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 discussions

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$_2$; (2) Bi$_{0.30}$U$_{0.70}$O$_2$; (3) Bi$_{0.32}$U$_{0.68}$O$_2$; (4) Bi$_{0.40}$U$_{0.60}$O$_2$; (5) Bi$_{0.50}$U$_{0.50}$O$_2$; (6) Bi$_{0.60}$U$_{0.40}$O$_1.95$; (7) Bi$_{0.65}$U$_{0.35}$O$_2$; (8) Bi$_{0.70}$U$_{0.30}$O$_{1.80}$; and (9) Bi$_{0.80}$U$_{0.20}$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 fluoride-type phases have been reported in the U$^\text{IV}$ system, UO$_2$-Bi$_2$O$_3$ over the entire compositional range by Hund.\textsuperscript{13} A non-linear variation of the lattice parameter has been observed, which was explained by the increase of anionic vacancies with increasing Bi$_2$O$_3$ content, assuming uranium remained at the oxidation state IV (Hund).\textsuperscript{13} 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.\textsuperscript{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, i.e. a random distribution of the two elements in space.

Only Bi$_{0.60}$U$_{0.40}$O$_{2.00}$ 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 the poor quality of the refinement in $Fm-3m$ 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. $C2$, $a=6.889(3)$ Å, $b=4.007(4)$ Å, $c=9.691(5)$ Å, $\beta=90.13(3)\textdegree$) strongly suggest the formation of the monoclinic form of the U$^\text{VI}$ compound $\alpha$-Bi$_2$UO$_5$.\textsuperscript{8-10} This hypothesis is at first quite surprising, having in mind the synthesis method (reaction of stoichiometric amounts of commercial $\alpha$-Bi$_2$O$_3$ oxide and UO$_2$ 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.

![Fig. 1 Lattice parameter variation in the Bi-U-O system as a function of the substitution degree. For Bi$_{0.60}$U$_{0.40}$O$_{2.00}$ (●), see discussions. Inset: XRD patterns of the different mixed oxides analysed in this study.](image)

**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>$\beta$, °</th>
<th>$V$, Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{0.15}$U$</em>{0.85}$O$_2$</td>
<td>5.463 (1)</td>
<td></td>
<td></td>
<td></td>
<td>163.04 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.30}$U$</em>{0.70}$O$_2$</td>
<td>5.465 (1)</td>
<td></td>
<td></td>
<td></td>
<td>163.22 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.32}$U$</em>{0.68}$O$_2$</td>
<td>5.467 (1)</td>
<td></td>
<td></td>
<td></td>
<td>163.40 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.40}$U$</em>{0.60}$O$_2$</td>
<td>5.472 (1)</td>
<td></td>
<td></td>
<td></td>
<td>163.85 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.50}$U$</em>{0.50}$O$_2$</td>
<td>5.478 (1)</td>
<td></td>
<td></td>
<td></td>
<td>164.35 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.60}$U$</em>{0.40}$O$_1.95$</td>
<td>5.516 (1)</td>
<td></td>
<td></td>
<td></td>
<td>167.83 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.65}$U$</em>{0.35}$O$_2$</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$</em>{0.30}$O$_{1.80}$</td>
<td>5.638 (1)</td>
<td></td>
<td></td>
<td></td>
<td>179.21 (3)</td>
</tr>
<tr>
<td>Bi$<em>{0.80}$U$</em>{0.20}$O$_{1.70}$</td>
<td>5.612 (1)</td>
<td></td>
<td></td>
<td></td>
<td>176.75 (3)</td>
</tr>
</tbody>
</table>

* The O/M ratios have been derived from the U molar fractions and XANES measurements.
Fig. 2 Rietveld refinement of the sample Bi0.65U0.35O2.00 using a monoclinic cell (S.G. C2) 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.

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. UVI02, (UVI)2O3, (UVI)3O8, and UIVO5. 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 reported here in we demonstrate that the uranium oxidation states can be characterized using the U MIV edge HR-XANES technique. The HR-XANES spectrum of UVI02 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 (UVI)2O3, (UVI)3O8 HR-XANES spectrum depicts a peak at the same energy position characteristic of UVI and also a peak at 3725.5 (2) eV which corresponds to UVII. The (UVI)3O8 HR-XANES spectrum exhibits a white line at 3726.2 (2) eV attributed to UVIII and a shoulder at the lower energy side with energy position characteristic for UIV. The energy positions of the white line of the UIV02 spectrum and the UVIII peak in (UVI)3O8 coincide (3726.2 (2) eV) and it is characteristic for UIV compounds.

Table 2 Uranium valence and molar fraction in the Bi-U-O compositions

<table>
<thead>
<tr>
<th>Chemical composition*</th>
<th>UIV</th>
<th>UVIII</th>
<th>UVI</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi0.15U0.85O2.00</td>
<td>82</td>
<td>18</td>
<td>0</td>
<td>0.005</td>
</tr>
<tr>
<td>Bi0.32U0.68O2.00</td>
<td>44</td>
<td>56</td>
<td>0</td>
<td>0.020</td>
</tr>
<tr>
<td>Bi0.50U0.50O2.00</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</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>0</td>
<td>100</td>
<td>0.006</td>
</tr>
<tr>
<td>Bi0.79U0.21O1.81</td>
<td>0</td>
<td>10</td>
<td>90</td>
<td>0.003</td>
</tr>
</tbody>
</table>

* The O/M ratios have been derived from the U molar fractions in respect of electroneutrality.

Fig. 3 U MIV XANES spectra of Bi-U-O compositions.

Except for Bi0.39U0.61O1.82, 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 Bi0.15U0.85O2.00 and Bi0.32U0.68O2.00 exhibit the two features characteristics of UIII and UVII. However, it can be observed that the amplitude of the UVI peak decreases with increasing the bismuth content.

Valence state of bismuth

XANES measurements at the Bi LIII have been performed to elucidate the bismuth valence state. The Figs. 4a and 4b present the Bi LIII XANES spectra of the Bi-U-O samples.
In the Bi L\textsubscript{III} XANES spectra, there is a shift toward higher energies between the Bi\textsuperscript{5+}O\texttextsubscript{2}, Bi\textsuperscript{3+}UO\textsubscript{2} and NaBi\textsuperscript{5+}O\textsubscript{2}xH\textsubscript{2}O white lines passing from Bi\textsuperscript{5+} to Bi\textsuperscript{3+}. Although bismuth is trivalent in both Bi\textsuperscript{3+}O\textsubscript{2} and Bi\textsuperscript{3+}UO\textsubscript{2}, the XANES spectra are different and shifted from one another. This has already been reported\textsuperscript{23} for other isovalent compounds and can be understood from the difference of local environment. The NaBi\textsuperscript{5+}O\textsubscript{2}xH\textsubscript{2}O spectrum exhibits a pre-edge describing 2p\textsubscript{3/2}-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 Bi\textsubscript{0.15}U\textsubscript{0.85}O\textsubscript{2:00}, Bi\textsubscript{0.32}U\textsubscript{0.68}O\textsubscript{2:00}, and Bi\textsubscript{0.50}U\textsubscript{0.50}O\textsubscript{2:00}, compositions have similar 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,\textsuperscript{34} 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 UO\textsubscript{2} 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\textsuperscript{-1}, which is assigned to the T\textsubscript{2g} anti-symmetric U\textsuperscript{VI}-O stretching vibration typical of eight-fold coordinated uranium in the fluorite structure. It has been observed many times in UO\textsubscript{2} and isomorphous compounds.\textsuperscript{25-30}

Factor group theory\textsuperscript{31} indicates that it is the only Raman active mode in the Fm-3m space group. As Bi\textsuperscript{3+} is dissolved in the UO\textsubscript{2x} lattice, this band broadens and its peak position shifts towards slightly higher energy.

![Fig. 4a Bi L\textsubscript{III} XANES spectra of Bi\textsubscript{0.15}U\textsubscript{0.85}O\textsubscript{2:00}, Bi\textsubscript{0.32}U\textsubscript{0.68}O\textsubscript{2:00}, Bi\textsubscript{0.50}U\textsubscript{0.50}O\textsubscript{2:00}, and Bi\textsubscript{0.61}U\textsubscript{0.40}O\textsubscript{1.95}.](image1)

![Fig. 4b Bi L\textsubscript{III} XANES spectra of Bi\textsubscript{0.61}U\textsubscript{0.40}O\textsubscript{1.95}, Bi\textsubscript{0.67}U\textsubscript{0.33}O\textsubscript{2:00}, Bi\textsubscript{0.76}U\textsubscript{0.24}O\textsubscript{1.81}, and Bi\textsubscript{0.81}U\textsubscript{0.15}O\textsubscript{1.70}.](image2)

![Fig. 5 Raman spectra of the Bi-U-O compositions.](image3)
630 cm\(^{-1}\) increases for Bi\(_{0.32}\)U\(_{0.68}\)O\(_{2}\)\(_{2.00}\) and Bi\(_{0.60}\)U\(_{0.40}\)O\(_{2}\)\(_{2.00}\), which is similar to observations for U\(_3\)O\(_8\). All of these observations are in agreement with the presence of mixed valence U\(^{VI}/U^{IV}\) 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 Bi\(_{0.60}\)U\(_{0.40}\)O\(_{2}\)\(_{1.95}\), Bi\(_{0.70}\)U\(_{0.30}\)O\(_{1.81}\) and Bi\(_{0.86}\)U\(_{0.14}\)O\(_{1.70}\). 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\(^{-1}\) (T\(_{2g}\)) broadens with increasing the bismuth content together with the appearance of weak features at low frequencies \(\sim 210\) cm\(^{-1}\) and 280 cm\(^{-1}\) (typically for Bi\(_{0.60}\)U\(_{0.40}\)O\(_{1.95}\) and Bi\(_{0.60}\)U\(_{0.33}\)O\(_{2}\)\(_{2.00}\)). These modes (at 210 cm\(^{-1}\) and 280 cm\(^{-1}\)) are also present in the Raman spectrum of Bi\(_2\)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 Bi\(_{0.67}\)U\(_{0.33}\)O\(_{2}\)\(_{2.00}\), a monoclinic phase.

Despite the clear distortion at local range and by analogy with the Raman spectra of U\(_3\)O\(_8\), UO\(_2\) and UO\(_2\)\(^{2+}\)\(_{32-33}\) the peak around 717 cm\(^{-1}\) can be attributed to a Raman active U-O stretching vibration of UO\(_8\) polyhedra with non-bonding oxygen in close geometry to the UO\(_2\)\(^{2+}\) species. This assignment agrees well with the Raman spectrum of the hexavalent uranium compound CaUO\(_6\)\(_{23}\) where this vibration was clearly identified as the v\(_1\) stretching mode of the uranyl 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 Bi\(_{0.62}\)U\(_{0.38}\)O\(_{2}\)\(_{2.00}\) and Bi\(_{0.50}\)U\(_{0.50}\)O\(_{2}\)\(_{2.00}\) displayed in Fig. 6, the T\(_{2g}\) band typical of the fluorite structure and oxygen defect bands between 570 and 630 cm\(^{-1}\).\(^{31}\) The latter lines are attributed to T\(_{4u}\) LO phonons Raman inactive in the absence of oxygen defects. They are not affected by Bi\(^{III}\) doping, suggesting that only the uranium (IV) atoms change to uranium(V) to compensate the electric charge on addition of Bi\(^{III}\). The T\(_{2g}\) band clearly dominates the spectrum of the uranium-rich samples suggesting that the fluorite 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 UO\(_8\) species with non-bonding oxygens (similar to uranyl ions).

Fig. 6 Raman spectra of Bi\(_{0.50}\)U\(_{0.50}\)O\(_{2}\)\(_{2.00}\), Bi\(_{0.32}\)U\(_{0.68}\)O\(_{2}\)\(_{2.00}\), and Bi\(_{0.67}\)U\(_{0.33}\)O\(_{2}\)\(_{2.00}\).

The spectrum of the pure U\(^{VI}\) phase Bi\(_{0.67}\)U\(_{0.33}\)O\(_{2}\)\(_{2.00}\) is even more strongly dominated by this latter line in agreement with the layer organisation of \(\alpha\)-Bi\(_2\)O\(_3\).

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

At 50 mol% of UO\(_2\) and Bi\(_2\)O\(_3\), a fluorite-type phase of general formula U\(_3\)Bi\(_2\)O\(_{5}\) (or BiUO\(_4\)) forms. The cell parameter 5.478(1) Å, is larger than UO\(_2\) (5.471 Å). This is consistent with the average ionic radii of Bi\(^{III}\)\(_{CN8}\) (1.17 Å) and U\(^{VI}\)\(_{CN8}\) (0.93 Å), with the former being slightly larger than ionic radius of U\(_{CN6}\)=1.00 Å. In U\(_3\)Bi\(_2\)O\(_5\) the average distance M-O is 2.372 Å. 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.

Fig. 7 Rietveld refinement of BiUO\(_4\). Comparison between the observed (Yobs, in red) and calculated (Ycalc, in black) X-ray diffraction pattern of BiUO\(_4\) phase. Yobs-Ycalc (in blue) is the difference between the experimental and calculated intensities. The Bragg reflections are marked in black ticks.
The evolution of the unit-cell volume of $X^{III}$UO$_4$ phases as a function of eight-fold coordinated cationic radius (Fig. 8) would confirm that BiUO$_4$ belongs to this family. Note that FeUO$_4$ and CrUO$_4$, not shown in this graph, are not cubic.  

For some of these $X^{III}$UO$_4$-type compositions ($X$= Bi, Sc, and Y), the pentavalent oxidation state of uranium was proven based on magnetic susceptibility measurements. This might be an indication that all the other $X^{III}$UO$_4$ compositions shown in this graph are pure pentavalent uranium phases.

### Table 3 Unit cell parameters and results of the Rietveld refinement for BiUO$_4$

<table>
<thead>
<tr>
<th>Formula unit</th>
<th>BiUO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>5.478 (1) Å</td>
</tr>
<tr>
<td>$V$</td>
<td>164.35 Å$^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$Fm-3m$ (Nº=225)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>Refined parameters</td>
<td>40</td>
</tr>
</tbody>
</table>

$R_p = \Sigma |y_i(\text{obs})-y_i(\text{calc})|/\Sigma y_i(\text{obs})$ ; $R_w = (\Sigma w_i |y_i(\text{obs})-y_i(\text{calc})|^2)/\Sigma w_i y_i(\text{obs})$ ; GOF = $R_p/R_w$

### Table 4 Atomic positions in the BiUO$_4$ compound

<table>
<thead>
<tr>
<th>Atom</th>
<th>Oxidation state</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{iso}$ (Å$^2$)</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>

Fig. 8 Evolution of the unit-cell volume of $X^{III}$UO$_4$ phases as a function of eight-fold coordinated cationic radius. The unit-cell volume values are taken from the literature, while for BiUO$_4$ the present result is shown.

The relative variation of the cell parameters of BiUO$_4$ and $\alpha$-Bi$_3$UO$_6$ with temperature is presented in Fig. 9. The transition temperature of $\alpha$-Bi$_3$UO$_6$ (C2 space group) to $\beta$-Bi$_3$UO$_6$ (P-3 space group) occurs between 600 and 800 °C, while the cubic BiUO$_4$ 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 UO$_2$ polyhedra (the thermal expansion along the $c$ axis is more pronounced because of the layer structure of $\alpha$-Bi$_3$UO$_6$). Trivalent bismuth, which is seven-fold coordinated, is poorly bonded to oxygen.

The linear thermal expansion (LTE) is defined as LTE$_{25°C}(T)=x(T)-x(25°C)/x(25°C)$. The polynomial interpolation of the experimental data are presented in Fig. 9 and gives for the cubic BiUO$_4$: LTE$_{25°C}(T)=-3.10^{-4}+1.47.10^{-9} T(°C) + 4.1.10^{-6} T^2(°C)$. Similarly, the LTE for the different orientations in Bi$_2$UO$_6$ are:

- $a$: LTE$_{25°C}(T)=-1.10^{-4}+3.2.10^{-6} T(°C) + 8.8.10^{-9} T^2(°C)$
- $b$: LTE$_{25°C}(T)=1.10^{-4} - 2.0.10^{-7} T(°C) + 8.2.10^{-9} T^2(°C)$
- $c$: LTE$_{25°C}(T)=-5.10^{-4}+1.65.10^{-5} T(°C)$

### 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 Hund has
been confirmed and its origin identified in the oxidation state of uranium. Even under inert atmosphere at 800 °C, UO₂ oxidises to U₂O₅ as a function of the substitution degree. We have identified the formation of the Bi₂UO₄ and Bi₂UO₅O₁₂ compounds, within this series. All the compositions crystallize in a fluorite-related structure, but the actual symmetry of Bi₂UO₅O₁₂ is monoclinic. Raman spectrometry indicates changes in the local symmetry from six-fold uranium coordination to an eight-fold coordination (deduced as a function 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

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Notes and references
