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Raman spectra of stoichiometric and hyperstoichiometric uranium dioxide

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Abstract

Raman spectra of stoichiometric and hyperstoichiometric uranium dioxide are presented, as measured on nuclear-grade UO_2 pellets treated under oxidising conditions to obtain different levels of hyperstoichiometry. The precipitation of higher oxides on the sample surface in contact with air, depending on the oxidation of the specimen, is observed. Modes revealing the formation on the surface of the compound U_3O_8, such as the line at 750 cm^{-1}, are detected in specimens with bulk O/U $\geqslant 2.09$. Particular attention is given to the behaviour of the line observed for stoichiometric UO_2 at 1151 cm^{-1}, attributed to the crystal electric field $\Gamma_5 \rightarrow \Gamma_3$ transition. According to the presented measurements, such line can be regarded as a fingerprint of the quasi-perfect fluorite structure. Results are discussed and compared with those of some previous publications results on the same subject.

1. Introduction

Micro-Raman spectroscopy is an effective technique in detecting chemical species although existing in traces only. In such a technique, high-quality Raman spectra are obtained from electromagnetic radiation scattered by very small material samples (the size of which can be as small as a few micrometers) after focusing an excitation-source laser beam on the sample surface through a standard optical microscope objective. This method has been successfully used to analyse microcrystalline precipitates and fluid inclusions in geological studies [1–3] as well as in applications concerning the nuclear fuel cycle. Within this latter field uranyl compounds have been particularly investigated since they occur as corrosion products stemming from nuclear waste leaching processes and since they exist in natural mineral formations too [4–7]. Micro-Raman spectroscopy has been widely used to characterise also uranium oxides [8–15] providing important information about the complex system uranium–oxygen, the knowledge of which is basic for the analysis of many stages of the nuclear fuel cycle.

The present work deals with micro-Raman spectroscopy measurements performed on uranium dioxide, one of the most studied materials ever, especially for its application as nuclear fuel. The main goals of such a study are the characterisation of peaks typical of the UO_{2+x} phase and the detection of possible higher oxide precipitations on the sample surface in contact with air when the oxygen content of the bulk matrix is increased by means of a suitable heat treatment.

Uranium dioxide crystallises in the fluorite structure, space group $Fm\bar{3}m$. Non-stoichiometry constitutes a particular feature of this compound. The species UO_{2+x} can exist, at sufficiently high temperature, in the form of a solid solution for approximately $-0.4 < x < +0.3$. Nonetheless, cubic fluorite-like symmetry is preserved

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up to $x = 0.25$ even at room temperature, where the excess oxygen atoms tend to cluster regularly, and to form precipitates with U_4O_9 composition and space group $I\bar{4}3d$, without affecting the symmetry of the uranium sublattice. In the case of the hypostoichiometric oxides ($x < 0$), vacancies in the normal oxygen sites are preponderant, whereas in the hyperstoichiometric region ($x > 0$) the oxygen-excess atoms are accommodated in octahedral interstitial sites. Such feature is allowed by the presence of a partially filled 5f shell in uranium and the possibility for a U atom to shift easily among the valencies +3, +4, +5 or +6.

Infrared spectra of stoichiometric and hyperstoichiometric uranium dioxide were measured by Allen et al. [16]; Raman spectra were measured by several authors on the stoichiometric compound [8–14], but data are still rather scarce for the non-stoichiometric compositions. An enhanced experimental data set on the lattice modes at oxidation states increasingly further from the exact stoichiometry is therefore needed for a better understanding of the crystalline system evolution as a function of the oxygen content.

2. Experimental

The characterised samples were nuclear grade standard UO_2 pellets, provided by the manufacturer as stoichiometric. Thermogravimetry, electromotive force and X-rays diffraction measurements were performed at the ITU in order to check the specimens actual composition, obtaining for it $UO_{2.000\pm0.005}$. Stoichiometric pellets were then treated in an alumina furnace at different temperatures under a CO/CO_2 oxidising gas flow of suitable composition in order to produce hyperstoichiometric samples according to the $UO_{2\pm x}$ Ellingham diagrams as reported by Lindemer and Besmann [17]. Samples with bulk O/U ratios 2.00, 2.05, 2.07, 2.09, 2.12 and 2.20 were produced and analysed. Raman spectra measured on these samples revealed that, in presence of air, U_3O_8 precipitated on the surface of the more oxidised specimens (O/U $\geqslant$ 2.09).

Micro-Raman spectra were measured at FZK-IFP. Measurements were performed using a Dilor XY Raman spectrometer with attached microscope. The excitation source was a 514 nm argon laser. Spectra were recorded with a liquid N_2 cooled silicon detector (256×1024 pixels). The specimen presented low thermal sensitivity. Additionally, the laser beam was adjusted (in power and focal spot diameter) in order to avoid any oxidation of the sample surface during the measurements. The total wavenumber range from $\approx$200 to $\approx$1250 cm^{-1} was covered by three overlapping measurements, each being an average of three 90 s scans. Measurements were repeated several times on the same sample to make sure that no oxidation occurred, and on different samples to check the reproducibility of the results. The characterisation was also repeated at different points on the same sample, in order to check the homogeneity of the investigated surface. Samples that resulted inhomogeneous were left out.

3. Results

Fig. 1 shows the spectra recorded. The spectra presented were FFT-smoothed and arbitrarily shifted in order to be more distinguishable at the sight.

The spectra change gradually as the oxygen content increases. Three typical lines are detected at about 232, 445 and 1151 cm^{-1} in specimens with bulk composition close to stoichiometry (bulk O/U < 2.09). The peak at 1151 cm^{-1} completely disappears at higher oxidation, where the superficial precipitation of higher oxides is likely to cover considerably the UO_{2+x} cubic structure. Such peak can therefore be considered as a fingerprint of the quasi-perfect fluorite structure. Raman spectra on stoichiometric $UO_{2.00}$ were measured at low temperature, down to 5 K, in order to better establish the nature of the 1151 cm^{-1} line (Fig. 2). The intensity of this peak is higher at low temperature, indicating that the line is not due to phonons, but is rather of electronic origin (see discussion in Section 4).

A broad peak of low intensity appears at 763 cm^{-1} for the $UO_{2.09}$ composition, and is visible with increased intensity, at about 750 cm^{-1}, in more oxidised samples. Lines in these samples can be identified at about 240 cm^{-1} and, for bulk O/U $\geqslant$ 2.12, about 330 cm^{-1}. A hardly visible line at 470–475 cm^{-1} for $UO_{2.09}$ and $UO_{2.12}$ is probably overlapped with other modes in $UO_{2.20}$. Lines are in general hardly distinguishable at wavelength <500 cm^{-1} in samples with bulk O/U > 2.09. Such behaviour is likely due to the fact that the spectra of hyperstoichiometric samples tend to be composites of the single spectra of different species, such as UO_2, U_4O_9, U_3O_7 and U_3O_8, as higher oxides are likely to precipitate in traces on the surface. If this happens, several peaks can overlap, covering each other.

4. Spectra description and discussion

A summary of the lines observed in this work with their attributions is compiled in Table 1. In the same table other authors' publications are also quoted, that report peaks similar to those observed in this work. A discussion on the attribution of each line, based on the comparison with literature references, is at this point suitable.

The peak that we recorded at (237 ± 5) cm^{-1} was previously recorded by Allen et al. [10] in fluorite-structured UO_2 samples, by Graves [13] in UO_2 samples

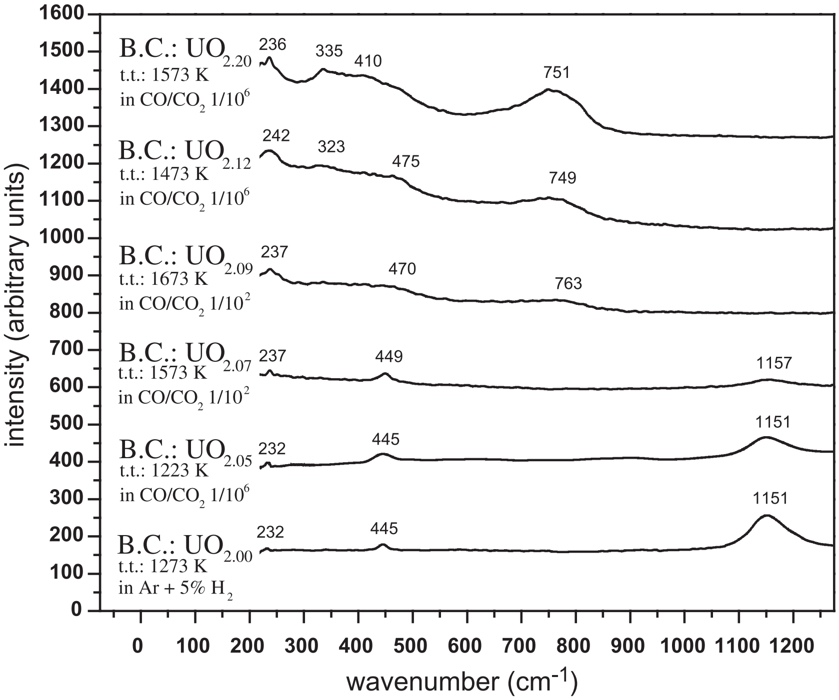

Fig. 1. Raman spectra measured on oxidised UO_{2+x} samples of several oxidation levels. Beside each spectrum are indicated the bulk composition (BC) of the corresponding specimen and the thermal treatment (tt) to which the specimen was subjected. The bulk composition corresponds to the composition of the surface in slightly oxidised samples (O/U $\leqslant$ 2.07). The superficial composition of more oxidised samples is unknown, due to the precipitation of higher oxides on the surface in contact with air.

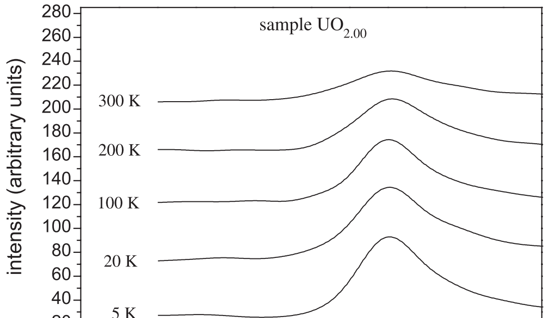

Fig. 2. Low temperature Raman spectra of stoichiometric UO_2 around 1000 cm^{-1}. The 1151 cm^{-1} line intensity is higher at low temperature, showing a behaviour proper of a lattice electric field transition. The sample was directly cooled by a stream of He gas in a continuous flow cryostat Optistat-CF manufactured by Oxford Instruments. The intensity of the peak at 300 K is lower than the one reported in Fig. 1 because the scattered light was significantly attenuated by the cryostat window.

implanted with Kr ions, and also, weaker, by Butler et al. [15] in orthorhombic U_3O_8 samples, but its origin is not fully clear. In fact, as Butler et al. stated, it was completely overlooked in the calculations. Also in our measurements this vibration was observed for stoichiometric UO_2 samples, and, stronger and stronger, for the more oxidised ones. One could reckon that either two different bands exist, one belonging to the fluorite structure, the other one to the orthorhombic structure, and that both should have frequencies in the range 230–245 cm^{-1}, or that there is a mode of vibration common to the two structures.

The peak observed by us at 335 cm^{-1} and at 323 cm^{-1} in samples with the highest oxidation levels could reasonably be considered as an underestimate of the line given by the A_{1g} U–O stretching vibration expected for the orthorhombic U_3O_8 lattice at 342 cm^{-1}, as calculated by Butler et al. It can reveal the presence, on the surface, of a certain amount of oxide U_3O_8 on the most oxidised samples.

The peak at 445 cm^{-1} is typical of the fluorite-structured UO_{2+x} close to stoichiometry, corresponding to the triply degenerate T_{2g} Raman-active vibration. The wavenumber at which we recorded such peak corresponds to the frequency given in the UO_2 neutron scattering spectrum presented in the work of Dolling et al. [18]. The same peak at the same frequency was measured in other publications too. Marlow et al. [8]

Table 1
Raman lines observed on stoichiometric and oxidised uranium dioxide specimens

Peaks observed in this work (cm^{-1})		Attribution	References
Stoichiometric or slightly oxidised uranium dioxide ($2.00 \leqslant O/U \leqslant 2.07$)	Strongly oxidised uranium dioxide ($2.09 \leqslant O/U \leqslant 2.20$)		
232		?	[10,13]
	≈237	U_3O_8 line of uncertain origin	[15]
	≈335	U_3O_8 A_{1g} U–O stretching	[14,15]
	≈410	U_3O_8 A_{1g} U–O stretching	[14,15]
	≈475	U_3O_8 E_g U–O stretching	[14,15]
445		UO_2 T_{2g} U–O stretching	[7–14,18]
	≈750	U_3O_8 combination of two A_{1g} O–U stretching bands ($335 + 410 = 745$)	[14,15]
1151		UO_2 $\Gamma_5 \rightarrow \Gamma_3$ CEF transition	[11–13,19–21]

measured the band at (445 ± 2) cm^{-1}, Keramidas and White [9] observed the same vibration for the three fluorite-structured oxides CeO_2, ThO_2 and UO_2 (stoichiometric), in the three cases at a wavenumber around 465 cm^{-1}. Graves [13] measured the same line from a typical uranium dioxide single-crystal at 448 cm^{-1}.

One sees from our spectra that the T_{2g} peak tends to broaden in more oxidised samples, as the ordered defect phase β-U_3O_7 is probably formed on the surface, and in this phase the T_{2g} mode splits into separate components [10]. At the highest oxidation level the line is possibly hidden by other peaks characteristic of the oxide U_3O_8, which has two Raman-active U–O stretching vibrations at ≈410 cm^{-1} (A_{1g}) and at ≈480 cm^{-1} (E_g) [14,15].

Characteristic of the orthorhombic U_3O_8 lattice is also the peak around 750 cm^{-1}, observed by us in the more oxidised samples. It was attributed to the composition of two A_{2u} O–U stretching vibrations in chain.

No mode was instead observed in this work about 810 cm^{-1}, where Palacios and Taylor [14] reported a vibration, previously mentioned by Butler et al. [15] too, associated in U_3O_8 with the octahedral UO_3 unit. In the same range the symmetric axial stretch of the uranyl ion produces a clear line in the vicinity of 800 cm^{-1}, the exact position of which depends upon the bonding situation of the uranyl group [7]. Uranyl compounds are actually likely to form in aqueous environment exposed to air, and their formation was therefore not expected on the samples investigated here.

The broad peak detected by us for stoichiometric and slightly oxidised (bulk $O/U < 2.09$) uranium dioxide samples about 1151 cm^{-1} is particularly interesting. Such a band can be regarded as a peculiar mode of the quasi-perfect UO_{2+x} fluorite structure.

Such peak was reported by Schoenes [11] by Blumenroeder et al. [12] and by Graves [13], and explained as a crystal electric field (CEF) transition, though the interpretation was not really definite. The peak observed by us is slightly asymmetric, like in the spectra measured by Schoenes and Graves, possibly indicating the presence of a weaker line between 1150 and 1200 cm^{-1}.

Schoenes [11] measured Raman spectra of UO_2 samples up to 2500 cm^{-1}, between 10 and 300 K. He observed a strong peak at 1145 cm^{-1}. As its intensity decreased with increasing temperature, the line was attributed to electronic rather than phonon scattering, probably to the $\Gamma_5 \rightarrow \Gamma_3$ CEF transition. Such a transition was measured through inelastic neutron scattering and analysed by Amoretti et al. [19] and by Kern et al. [20] and was recently recalculated on the basis of available experimental data by Rahman [21]. However, Schoenes could not explain why the strong line observed in the Raman scattering spectrum never appeared in the absorption IR spectrum. The question was left open, suggesting that also phonon-assisted crystal-field transitions should be considered. Blumenroeder et al. [12] also assigned the peak observed at ≈1150 cm^{-1} to the $\Gamma_5 \rightarrow \Gamma_3$ CEF transition, being the corresponding CEF levels scheme in agreement with their magnetic susceptibility temperature dependence measurements.

Graves' micro-Raman measurements of a urania single-crystal [13] showed in the XX polarised spectrum a broad peak at 1156 cm^{-1}, and in the XY depolarised spectrum two weaker off-diagonal bands associated to it at 1104 and 1152 cm^{-1}. Since there are no components with both diagonal and off-diagonal elements in the cubic space group tensors, the observation of off-diagonal peaks in the XY spectrum excluded the possibility to attribute the mode to any phonon process. Therefore Graves attributed the 1156 cm^{-1} line to electronic scattering.

Palacios and Taylor [14] recorded stoichiometric UO_2 spectra up to 4000 cm^{-1}, but they presented them up to 1000 cm^{-1} only, as they did not detect any peak of interest at higher wavenumbers. It would be interesting to know whether the $\approx$1150 cm^{-1} peak was actually not recorded, not considered, or simply overlooked by these authors.

Our already mentioned spectra measured on stoichiometric UO_2 at 200, 100, 20 and 5 K (Fig. 2) show that the 1151 cm^{-1} line intensity is higher at low temperature just like in the spectra presented by Schoenes [11]. This confirms that such a line should be attributed to electronic scattering rather than to a fluorite-like lattice vibrating mode.

While considering the results presented here, one should not forget that the exact composition of the samples surface is unknown, at least in samples with $O/U > 2.09$, due to the precipitation of higher oxides, that occurs as the specimens are kept in contact with air. On the other hand, even in absence of precipitates, uranium dioxide with $O/U < 2.09$ exists at room temperature as a mixture of two phases, UO_{2+x} and U_4O_{9-y}. Nonetheless, spectra measured in this work change regularly with the oxygen content of the bulk, which is well known, and the trend shown is certainly useful in identifying different oxidation levels in hyperstoichiometric uranium dioxide samples in contact with air. Moreover, the oxygen content dependent fade of the 1151 cm^{-1} line can interestingly be connected, though the change in the CEF levels scheme, with the gradual variation of uranium mean valency due to increasing oxidation in the lattice.

5. Conclusions

The present work demonstrates that micro-Raman spectroscopy can successfully be used to detect specific features in the excitation spectra of UO_{2+x} samples with different oxidation level. The method could also reveal the formation of higher oxides on the sample surface in contact with air.

The peak found in stoichiometric and slightly hyperstoichiometric (bulk $O/U < 2.09$) uranium dioxide at 1151 cm^{-1} is attributed to a $\Gamma_5 \rightarrow \Gamma_3$ CEF transition. It can be regarded as a fingerprint of the quasi-perfect fluorite structure, along with the vibrational T_{2g} line measured at 445 cm^{-1}. The behaviour shown by the 1151 cm^{-1} peak upon enrichment in oxygen provides information, to be considered in a more theoretical study, on the variation of the uranium mean valency in the lattice.

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References

[1] P. Dhamelincourt, J.M. Beny, J. Dubessy, B. Poty, Bull. Mineral. 102 (1979) 600.

[2] J. Dubessy, A. Audeoud, R. Wilkins, C. Kosztolanyi, Chem. Geol. 37 (1982) 67.

[3] J.D. Pasteris, B. Wopenka, J.C. Seitz, Geochim. Cosmochim. Acta 52 (1988) 979.

[4] B.S.M. Rao, E. Ganter, J. Reinhart, D. Steinert, H.J. Ache, J. Nucl. Mater. 170 (1990) 39.

[5] B.M. Biwer, W.L. Ebert, J.K. Bates, J. Nucl. Mater. 175 (1990) 188.

[6] D.E. Morris, P.G. Allen, J.M. Berg, C.J. Chisholm-Brause, S.D. Conradson, R.J. Donhoe, N.J. Hess, J.A. Musgrave, C.D. Tait, Environ. Sci. Technol. 30 (1996) 2322.

[7] M. Amme, B. Renker, B. Schmid, M.P. Feth, H. Bertagnolli, W. Döbelin, J. Nucl. Mater. 306 (2002) 202.

[8] P.G. Marlow, J.P. Russel, J.R. Hardy, Philos. Mag. 14 (1966) 409.

[9] V.G. Keramidas, W.B. White, J. Chem. Phys. 59 (1973) 1561.

[10] G.C. Allen, I.S. Butler, N.A. Tuan, J. Nucl. Mater. 144 (1987) 17.

[11] J. Schoenes, J. Chem. Soc., Faraday Trans. 2 (83) (1987) 1205.

[12] S. Blumenroeder, H. Brenten, E. Zirngiebl, R. Mock, G. Guentherodt, J.D. Thompson, Z. Fisk, J. Naegele, J. Magn. Magn. Mater. 76&77 (1988) 331.

[13] P.R. Graves, Appl. Spectrosc. 44 (1990) 1665.

[14] M.L. Palacios, S.H. Taylor, Appl. Spectrosc. 54 (2000) 1372.

[15] I.S. Butler, G.C. Allen, N.A. Tuan, Appl. Spectrosc. 42 (1988) 901.

[16] G.C. Allen, J.A. Crofts, A.J. Griffiths, J. Nucl. Mater. 62 (1976) 273.

[17] T.B. Lindemer, T.M. Besmann, J. Nucl. Mater. 130 (1985) 473.

[18] G. Dolling, R.A. Cowley, A.D.B. Woods, Can. J. Phys. 43 (1965) 1397.

[19] G. Amoretti, A. Blaise, R. Caciuffo, J.M. Fournier, M.T. Hutchings, R. Osborn, A.D. Taylor, Phys. Rev. B 40 (1989) 1856.

[20] S. Kern, C.-K. Loong, G.H. Lander, Phys. Rev. B 32 (1985) 3051.

[21] H.U. Rahman, Phys. Lett. A 240 (1998) 306.