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# Raman study of the oxidation in (U, Pu)$O_2$ as a function of Pu content

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## HIGHLIGHTS

- Raman spectroscopy is highly reliable for evaluating the (U, Pu)$O_2$ fuel oxidation.
- The higher the Pu content, the more the oxidation of the dioxide matrix is hindered.
- $M_4O_9$ is the intermediate stable phase found before oxidising to $M_3O_8$ (M = U, Pu).

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## ABSTRACT

This work presents a systematic Raman study of the matrix oxidation in a variety of $(U_{1-y}, Pu_y)O_2$ compositions ($0 \leq y \leq 0.46$) at different temperatures, between 250 °C and 400 °C. Our results indicate that the increase in Pu content hinders the oxidation process of the dioxide matrix. Further oxidation of the uranium-plutonium mixed dioxides in air starts between 250 °C and 310 °C, on a time scale of several hours. $M_4O_9$ seems to be the most stable intermediate phase formed upon oxidation of all the investigated mixed oxides, before final oxidation to $M_3O_8$. In addition, X-ray diffraction measurements and SEM images confirm the trend observed by Raman spectroscopy, *i.e.* Pu stabilises the fcc structure of the dioxide.

## 1. Introduction

The performance assessment of spent nuclear fuel (SNF) stability under dry interim storage conditions is of great importance in nuclear waste technology. In case of failure of the engineered containment barriers, oxidation of the spent fuel matrix ($UO_2$) might take place depending on the oxygen concentration in the surroundings and the temperature produced by the decay heat. As is well known, oxidation of $UO_2$ to $U_3O_8$ involves an increase in volume of around 36% that might affect fuel integrity and, consequently, storage safety [1]. Hence, it becomes necessary to understand in detail how this reaction proceeds, analysing step-by-step not only the different uranium oxides that take part in the oxidation, but also the reaction mechanisms responsible for the consecutive structural transitions along the $UO_2 \rightarrow U_4O_9/U_3O_7 \rightarrow U_3O_8$ transformation [2].

In particular, the first stage of the latter reaction, *i.e.* $UO_2$ evolution to $U_4O_9/U_3O_7$, takes on special interest owing to the fact that various crystal symmetry transitions occur along this compositional range while the overall structure remains cubic [3]. Such transitions have been experimentally detected by means of Raman spectroscopy and X-ray diffraction (XRD) [4,5]. As additional oxygen atoms are incorporated into the *Fm-3m* cubic lattice, they continuously rearrange without altering it in a significant way, eventually giving rise to a so-called superstructure. This corresponds to the $U_4O_9$ phase, which consists of a very densely packed cubic structure where oxygen atoms arrange themselves into cuboctahedral clusters [6]. Likewise, $U_3O_7$ has a distorted cubic lattice, only differing from $U_4O_9$ in the slight alteration caused by the excess of oxygen [3].

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Full comprehension of this oxidation reaction becomes even a greater challenge when, instead of dealing with pure uranium dioxide, it concerns uranium-based mixed oxides like (U, Pu)$O_2$, commonly referred to as MOX, and (U, Am)$O_{2-x}$. Such is the case of the potential fuels for fast neutron reactors, mainly intended for nuclear waste radiotoxicity reduction. In this sense, it is certainly necessary to assess the behaviour of the transuranium elements within the $UO_2$ matrix and their influence in the stability of this kind of SNF against oxidation/corrosion during storage.

Especially, the effect of Pu incorporation into the $UO_2$ matrix has been frequently addressed, since MOX fuels have been used for at least 30 years in some countries, *e.g.* France, Belgium or Germany, with the aim of recycling Pu in Light Water (thermal) Reactors (LWR) [7]. In this way, $(U_{1-y}, Pu_y)O_2$ oxides with different $y$ values as well as a few spent MOX fuels have been characterised and their oxidation in some cases investigated [8–21]. In these studies, a variety of experimental techniques have been employed, although XRD is by far the most frequent. Already in the 1970s, XRD measurements were applied for analysing the oxidation products of uranium-plutonium mixed oxides obtained in a thermal balance [8,9]. More recently, the effect of Pu content on the mixed dioxide lattice parameter at room temperature and the structure evolution after oxidation have been assessed [10–17]. In all of them the lattice parameter has been reported to follow Vegard's law, decreasing linearly as a function of plutonium concentration. With regard to oxidation of $(U_{1-y}, Pu_y)O_2$ oxides at different temperatures, it has been found that Pu stabilises the cubic phase during the reaction and that the temperature of $M_3O_8$ formation is higher as Pu content increases [15].

Furthermore, Raman spectroscopy of nuclear materials and actinide compounds has been broadly developed in the last decade [4,5,18–34]. This is not only due to advances in Raman spectroscopy approaches, their versatility, and potential non-contact analyses, but also to the improvement of confinement techniques for highly radioactive materials [21,30,31], which have allowed the study of hazardous compounds practically unexplored until the last decade of the Twentieth Century.

Concerning uranium-plutonium mixed oxides, certain studies have provided Raman characterisation of both unirradiated samples and spent fuels corresponding to different Pu contents [18–22]. A higher oxidation resistance of this kind of mixed dioxides as Pu concentration increases has also been reported [20,21].

Nevertheless, none of these studies has systematically evaluated, directly by Raman spectroscopy, the matrix oxidation of (U, Pu)$O_2$ mixed oxides under different temperature conditions and as a function of Pu content. Such a detailed Raman analysis of the matrix oxidation, within a varying range of Pu concentrations, is presented here for the first time.

## 2. Experimental

### 2.1. Materials

A variety of starting $(U_{1-y}, Pu_y)O_2$ fragments, averaging 1-3 mm in surface size, with different Pu contents ranging from $y = 0$ up to $y = 0.46$ were used in this work. Some of them were provided by CEA (Commissariat à l'Energie Atomique, France) and others by JRC-Karlsruhe (Joint Research Centre, Germany). CEA samples were prepared and characterised by a well established powder metallurgy procedure described in previous publications [17]. JRC samples were prepared by sintering powders produced by sol-gel technique, as described elsewhere [22]. Table 1 comprises data concerning the samples, such as the *MOX* reference utilised hereafter for each one, the proportion of Pu they contain and their provider.

**Table 1**
List of (U, Pu)$O_2$ mixed oxides used in this work.

| Reference | Pu Content (mol%) (±2) | Provider |
|---|---|---|
| $UO_2$ | 0 | JRC |
| MOX 3.7 | 3.7 | JRC |
| MOX 14 | 14 | CEA |
| MOX 19 | 19 | CEA |
| MOX 35 | 35 | CEA |
| MOX 46 | 46 | CEA |

### 2.2. Sample preparation

Starting samples listed in Table 1 were annealed at 1600 °C during 15 min under reducing conditions (Ar + 6.5% $H_2$ flow), enabling the removal of lattice defects expected from alpha self-irradiation. Thereafter, the oxidation procedure consisted in heating them at a constant rate of 10 °C/min up to a given temperature in each experiment, *i.e.* 250, 310, 340 and 400 °C, under a synthetic air flow and maintaining the selected temperature for 3 h. The samples were withdrawn immediately after this time period elapsed, with the aim of avoiding further oxidation due to the slow inertial cooling of the furnace tube. Both annealing and oxidation experiments were carried out in an alumina tube furnace.

### 2.3. Raman spectroscopy

Due to the radioactivity of the MOX samples, it was necessary to encapsulate them prior to Raman spectra measurements into $\alpha$-shielding Plexiglas capsules recently designed and developed by JRC-Karlsruhe [31]. The spectra were recorded through the quartz window on top of these capsules.

Raman measurements were performed with a Jobin-Yvon T 64000 spectrometer. All spectra were acquired at an excitation wavelength of 647 nm, provided by a $Kr^+$ laser. The laser beam was focused on the sample through a long focal distance objective (NA (*Numerical Aperture*) = 0.5) with 50× magnification. The excitation power was optimised between 50 and 100 mW (being around 5 times lower at the sample surface [29]) in order to prevent further oxidation of the samples by the laser. The scattered radiation was dispersed using a 1800 grooves/mm holographic grating and recorded by a liquid-nitrogen cooled CCD detector. The single spectrograph configuration applied enabled a spectral resolution of $\pm 1\ cm^{-1}$. The spectrometer was daily calibrated using the $T_{2g}$ phonon ($520.5\ cm^{-1}$) of a silicon single crystal [35].

### 2.4. X-ray diffraction

XRD analyses were performed on crushed samples. About 20 mg of powder were loaded in an epoxy resin to avoid excessive dispersion of radioactive powder. A Seifert XRD-3003 X-ray diffractometer (Cu K$\alpha$ radiation) with a Bragg-Brentano $\theta/\theta$ configuration was used for the analyses. The device is implemented in a glove-box for radioactive material confinement. The powder patterns were recorded using a step size of 0.02° across the angular range $10° \leq 2\theta \leq 120°$. Structural analyses were performed by the Rietveld method using Jana2006 software [36]. Peak-profile analysis was carried out using pseudo-Voigt bandshapes.

### 2.5. Scanning electron microscopy

The scanning electron microscopy used in this work is a Philips XL40 SEM (Philips, Amsterdam, Netherlands), which has been modified in order to be used for the examination of highly active or irradiated nuclear materials [37,38]: the chamber, column,