Laser-induced oxidation of UO_2: A Raman study

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ABSTRACT

A reliable method to probe and characterise the oxidation of actinide oxides by means of Raman spectroscopy is introduced. The present so-called Raman Laser Heating method enables studying the behaviour of various compounds at high temperatures and under a given atmosphere with the unique alteration of a small amount of sample, which is certainly advantageous in terms of safety when handling hazardous or radioactive materials. The approach is based on a dual use of the laser beam, which is at the same time employed as excitation source for the Raman analysis and as heating source, by exploiting the possibility to vary the beam power density reaching the sample surface. A high laser power density can lead to a significant increase of the analyte surface temperature by up to several hundred of degrees. A sufficiently low power density allows us to subsequently acquire the corresponding Raman spectrum at the same point without distorting the measurement. In this work, UO_2 powder has been subjected to Raman Laser Heating in air as a proof of this method's applicability, attaining a sequential acquisition of the characteristic Raman spectra of the different oxides involved in the oxidation from UO_2 to U_3O_8. The temperature at which such sequence of phase transformations started to occur was estimated to be around (560 ± 40) K. The temperature at the sample surface was estimated from the Stokes/anti-Stokes intensities ratio, using a similar set-up to that used in the Raman Laser Heating experiments. These results are particularly appealing in remote analyses, like those required in the study of nuclear fuel and nuclear waste.

KEYWORDS

Laser Heating, Uranium Dioxide, Oxidation, Temperature Estimation

1. INTRODUCTION

Knowledge of the structure and reactivity of actinide oxides, AnO_2, is required for designing safe storages for spent nuclear fuel (SNF). Different efforts have been performed in this regard, studying the stability of the SNF under repository conditions or assessing its behaviour under possible accident scenarios.[1-4] From these studies it is well-known that the oxidation of UO_2 (SNF matrix) and other actinides present in the SNF (Np, Pu, Am, etc.) will influence the overall stability of the spent fuel pellets.

Oxidation of AnO_2 occurs via oxygen incorporation into the fluorite structure (fcc) of the stoichiometric oxide, which has alternating empty and occupied oxygen cubic sites. These vacancies facilitate oxidation, *e.g.* uranium dioxide can oxidise to UO_{2+x}, ($x < 0.25$) maintaining the fcc structure.[5,6] Further oxidation to higher oxidation states (V and VI) is also possible for uranium, leading to different structures such as the tetragonal or orthorhombic structures found for U_3O_7 and U_3O_8, respectively.[7]

Although oxidation of AnO_2 has been broadly studied for some actinides, such as U and Pu, some aspects of their structure and reactivity are still under debate. For instance, the exact hyperstoichiometry limits of UO_{2+x} in equilibrium with air, or the reactivity of allegedly hypervalent PuO_{2+x} (with additional atoms within the host lattice).[8-12] Therefore, additional studies are necessary in this regard, but the intense radiation field inherently associated to these materials makes it difficult to study them in safe conditions.

Raman spectroscopy is an analytical tool that has been established in recent years as a reliable probe for this kind of studies, as confirmed by the large increase in the specialised literature.[13-29] This is due to some of its features, as that 1) it does not require any special preparation of the sample, 2) the technique allows the analysis of a very small amount of sample, 3) it requires no direct contact between the experimental set-up and the analyte, 4) it can be easily implemented (remote analysis, Raman probes, handheld systems, etc.)

for different applications, and 5) controlling the excitation laser power density, it is a non-destructive technique.

The effects of the laser power density provided during a Raman measurement and its associated heating have been studied in detail on semi-conducting and insulating materials,[30-32] especially those showing a good absorption in the visible range. Actinide dioxides, and precisely UO_2, being a good absorber in the range of 1.9–2.5 eV,[33] belong to materials where care needs to be taken when conducting Raman experiments. Owing to AnO_2 absorption profiles, the local spot temperature may increase by hundreds of degrees. This causes several changes in the Raman modes and, sometimes, the sample alteration as a result of effects such as oxidation, photo-reduction, order-disorder transition, phase transition or decomposition.

Despite the fact that this heating action of the laser has been traditionally considered an inconvenience when it comes to perform Raman measurements, as the power is usually optimised to avoid sample alteration, some authors have taken advantage of this feature for various purposes. On the one hand, detailed Raman studies have recently been performed on PuO_2, NpO_2 and AmO_2, aimed primarily at the complete mode assignment of the observed Raman bands.[18,24,25,27] In order to solve some discrepancies in the reported nature of peaks and their origin, a study of the evolution of their spectra as a function of laser power density has been carried out. It has been shown that increasing the laser power density enhances the anharmonic behaviour of the T_{2g} mode in NpO_2 and PuO_2,[25,27] decoupling of the (Γ_8, LO–TO) bound state in NpO_2[25] and, finally, depopulation of $\Gamma_1 \rightarrow \Gamma_5$ and $\Gamma_1 \rightarrow \Gamma_3$ electronic crystal field excitations in PuO_2.[27] However, no phase alteration has been detected in these materials, even at temperatures above 700 K. On the contrary, in AmO_2 it has been observed that, even at very low power density, the laser may induce an unavoidable photolysis process when visible lasers are used, resulting in the formation of hyperstoichiometric americium sesquioxide Am_2O_{3+z}.[24]

On the other hand, laser heating has been employed for analysing the oxidation behaviour and/or resistance of uranium-based materials such as (U, Pu)O_2,[14,28] (U, La)O_2,[23] and even spent fuels.[22] In these studies, oxidation of the samples to higher oxidation-state phases has been observed by Raman spectroscopy, using the laser as a heat source.

Due to the feasibility of this laser-induced heating, the associated temperature estimation has become an attractive target. In a recent study, Naji *et al.*[27] verified that the analysis of the Stokes/anti-Stokes intensities ratio is a reliable method for the temperature estimation in this type of experiments. Thus, in this work we present a new *in situ* approach based on the simultaneous application of the laser-induced heating to gradually oxidise UO_2, and the corresponding temperature estimation by the Stokes/anti-Stokes analysis. The attained sequential oxidation under the laser beam, which has been for the first time systematically studied, is in good agreement with previously reported observations on UO_2 oxidation. The estimated temperature also seems to be consistent with existing literature data.

This paper has been organised as follows. The “Materials and methods” section describes the employed materials, the equipment, and the Raman Laser Heating method in detail. In the “Results and discussion” section, oxidation of UO_2 is shown as an example of the applicability of this method and, in addition, the Stokes/anti-Stokes spectral analysis is carried out in order to estimate the temperature at which phase transformations start to occur.

2. MATERIALS AND METHODS

Materials

UO_2 powder with a particle size distribution of ~15 µm, measured by dynamic light scattering (DLS), was annealed at 800ºC during 24 hours under reducing conditions (N_2:H_2 4:96 v/v) in order to ensure stoichiometric $UO_{2.00}$ was attained. Initial characterisation carried out on this powder is further described in the "Sample pre-characterisation" section.

Pre-characterisation techniques

Thermogravimetric experiments were conducted with a Q50 thermo-balance (TA Instruments, Spain) in synthetic air with a constant rate of 60 mL/min from room temperature up to 973 K, at a 10 K/min rate.

X-ray diffraction (XRD) characterisation was performed by means of a Philips PANalytical X'Pert MPD diffractometer using Cu K_α radiation (λ=1.54056 Å) and operating at 45 kV and 40 mA. Bragg-Brentano configuration geometry was used.

For the acquisition of scanning electron microscopy (SEM) images of the initial sample, a SU6600 (HITACHI) microscope was employed. Its ZrO/W electron cannon permits working with an accelerating voltage that covers from 0.5 to 30kV and with a magnification range from 10x up to 600000x.

Raman spectrometers

Raman spectroscopy analyses were mainly carried out at CIEMAT facilities (www.ciemat.es) using a Horiba LabRAM HR Evolution spectrometer (Jobin-Yvon Technology). A red laser of He-Ne with a wavelength of 632.8 nm (1.96 eV) and a nominal power of 20 mW (adjustable by filters) was used as the excitation source. The laser was focused onto the sample surface using a 100x objective (NA (*Numerical Aperture*) = 0.9) which led to a beam diameter of ~0.9 mm; the scattered light was then collected with the same objective, dispersed with a 600 grooves/mm grating, and finally detected with a Peltier-cooled CCD detector (256 x 1024 pixels).

Stokes/anti-Stokes Raman spectra were acquired using the Raman facility available at the European Commission's Joint Research Centre of Karlsruhe (https://ec.europa.eu/jrc/en/about/jrc-site/karlsruhe). It consists in a Jobin-Yvon T64000 spectrometer equipped with a 1800 grooves/mm grating and a low noise liquid nitrogen cooled Symphony CCD detector. The spectrometer was used in the triple stage mode, which permits access to both Stokes and anti-Stokes spectrum lines while blocking the elastic Rayleigh line. The excitation source used in this case was the 647 nm (1.91 eV) line of a Kr^+ laser with a controllable nominal power up to 0.5 W. The laser was focused using a 50x long focal objective (NA = 0.5) which led to a beam diameter of ~12.2 mm, and the power density impinging on the sample surface was measured by a Coherent® power-meter placed at a position corresponding to the sample surface.

Raman Laser Heating

Lasers can induce a local temperature increase, by up to several hundreds of degrees, if they are focused on a small spot. Therefore, the excitation source of the Raman spectrometer focused on UO_2 powder can increase its temperature and thereby, subjecting it to Laser Heating in air, it is possible to produce the conditions under which oxidation of this material takes place, *i.e.* O_2 (g) and high temperature. In practice, the method consists in first heating a selected particle of UO_2 by applying the excitation laser at high power density, thus inducing oxidation. Actually, a sequential oxidation can be attained setting the appropriate parameters: the laser power density at the sample surface, and the heating time or spectrum acquisition (as if we were in the course of a Raman experiment). After each heating step, the spectrum corresponding to the obtained oxide can be subsequently acquired at low power density, enabling the characterisation of the UO_2 phase transitions and the oxidation evolution.

3. RESULTS AND DISCUSSION

Sample pre-characterisation

UO_2 powder was analysed previous to the laser heating experiments by a variety of characterisation techniques: scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and thermogravimetric analysis (see Fig. S1 (Supporting Information)). The results obtained from this pre-characterisation confirmed the quasi-stoichiometry of the initial UO_2 sample.

Sequential oxidation by laser

First of all, in order to check that a sequential oxidation of UO_2 was actually feasible with the Raman set-up available at CIEMAT, several combinations of laser power densities and exposure times were performed. In this way, varying both parameters consecutively until a significant change in the spectrum was detected, an *in situ* sequential oxidation of a UO_2 particle was attained. Fig. 1 gathers some of the Raman spectra acquired during this oxidation reaction.

The bottom spectrum in Fig. 1 corresponds to the initial quasi-stoichiometric UO_2 (see Supplementary Information for further detail), featuring the T_{2g} band around 445 cm^{-1} and the 2LO mode band at ~1150 cm^{-1}.[34,35] Once oxidation started and additional oxygen was incorporated into the cubic structure of UO_2 (UO_{2+x}), a broad band appeared at 500-700 cm^{-1}. This contribution is commonly attributed to different structure defects.[13,16,26,36] As progressive oxidation occurred, the latter feature grew and the band at 1150 cm^{-1} decreased,[13,26,37] even disappearing when U_4O_9 was reached,[17] as can be observed in Fig. 1. At this point, a new band appeared at ~ 160 cm^{-1}, which is also characteristic of the U_4O_9 phase.[17] Further oxidation produced a marked change in the spectrum: the band at 445 cm^{-1} began to split, the band at 500-700 cm^{-1} decreased and two new bands at ~ 235 cm^{-1} and ~ 812 cm^{-1} appeared. This was possibly due to the increasing presence of orthorhombic U_3O_8. Finally, three bands in the range of 300-500 cm^{-1} and the ~ 235 cm^{-1} and ~ 812 cm^{-1} features indicated that a complete conversion to U_3O_8 had been accomplished.[15,38-41]

Thereafter, the appropriate laser power density and time parameters for the direct attainment of the two phase transformations ($UO_2 \rightarrow U_4O_9 \rightarrow U_3O_8$) were tested. Fig. 2 reflects the results of this Raman Laser Heating experiment, applied again to a UO_2 particle. The initial UO_2 spectrum is shown in Fig. 2a. By heating the sample surface during 5 seconds with a power density of 340 mW/cm^2 –measured at the sample surface and being lower by a factor 2 with regard to the output power density– provided by the red laser (632.8 nm), the spectrum shown in Fig. 2b was obtained, which corresponds to the typical spectrum of the intermediate U_4O_9 phase.[17] Then, using the same laser power density and a heating time of 10 seconds, a spectrum similar to that characteristic of U_3O_8 was acquired (see Fig. 2c).[15,38-41]

Reproducibility of this Raman Laser Heating protocol for UO_2 was ensured by heating different particles of similar sizes. The good reproducibility obtained between different measurements allows us to estimate the temperature conditions under which $UO_2 \rightarrow U_4O_9 \rightarrow U_3O_8$ phase transitions take place as a result of the laser-induced heating. It should be noted that this temperature value is strongly dependent on the roughness/grain size of the sample. Thus, the temperature at which these transitions occur can be better inferred by establishing a direct relation between the laser power density and the laser-induced temperature, by performing the Stokes/anti-Stokes analysis as hereafter described.

Stokes/anti-Stokes temperature analysis

The temperature of the laser-heated sample surface at which the transformations started to occur was estimated by evaluating the ratio between the T_{2g} Stokes and anti-Stokes

Raman intensities and using the following equation (Eqn (1)), based on the Boltzmann distribution of modes between energy levels,

$$\frac{I_{anti-Stokes}}{I_{Stokes}} = \left(\frac{\nu_0 + \nu_j}{\nu_0 - \nu_j}\right)^4 e^{-\frac{hc\nu_j}{k_B T}} \tag{1}$$

where ν_0 and ν_j are the wavenumbers of the excitation line and the Raman modes, respectively, $I_{anti\text{-}Stokes}$ and I_{Stokes} are the intensities of the anti-Stokes and Stokes Raman peaks, k_B is the Boltzmann constant, c is the speed of light, and T is the temperature. The estimated uncertainty was obtained by applying the method previously published by LaPlant *et al.*[42] This method was shown to give satisfactory results as compared by Naji *et al.*[27] for a PuO_2 sample which was externally heated in a Linkam TS1500 temperature stage.

The Raman anti-Stokes spectrum, however, can only be measured with a spectrometer equipped with a triple-mode optical path or any other system for which the use of high-pass filters is not required. Since these conditions are not met with the current Raman equipment at CIEMAT, the latter experiments were performed using the Raman facility available at the European Commission's Joint Research Centre of Karlsruhe (Germany). Thus, the absolute Stokes/anti-Stokes temperature (T_{SAS}) was derived from the ratio (R_{SAS}) between the experimental integrated intensities of the anti-Stokes and Stokes T_{2g} peaks. It should be pointed out that the T_{SAS} determination based on the T_{2g} peak intensity can only be rigorously performed as far as the original fluorite structure and T_{2g} mode features are maintained. Prior to these calculations, Stokes and anti-Stokes Raman spectra were corrected for the instrumental response according to the procedure described elsewhere. [27,32] Despite the instrumental correction, the value of T_{SAS} can represent the real sample temperature in a rather inaccurate fashion, due to uncontrollable sample-dependent factors affecting the intensities of the Stokes and anti-Stokes lines, such as defect or impurity fluorescence, roughness scattering, etc. Therefore, the value of T_{SAS}

should be considered as only indicative of the absolute temperature produced by the laser beam on the irradiated spot. In addition, although it is not the case, it should be noted that for this kind of analysis two important precautions need to be always taken into account with regard to the wavelength used: the assurance of no Raman resonance effects and the knowledge of the absorption behaviour of the material in that corresponding energy range. Raman spectra on UO_2 powder were measured in this case using the 647 nm line of a Kr^+ laser. Longer acquisition times (several tens of seconds) were however needed in order to resolve the anti-Stokes spectrum with the triple optical path. The resulting Raman spectra measured at different laser power density levels and the corresponding SAS temperatures are reported in Fig. 3a and Fig. 3b, respectively.

The power density levels reflected in Fig. 3 were measured at the exit of the laser cavity. The laser power density impinging on the sample surface was measured to be lower by a factor 5 approximately. The spectra measured correspond to defective fcc UO_2, showing a broad feature between 550 cm^{-1} and 630 cm^{-1} characteristic of UO_{2+x}.[13,16,26,36] This feature is observed up to ~68 mW/cm^2. Around this laser power density defect modes quickly disappear, and then U_3O_8 spectrum[15,38-41] is observed for higher laser power densities (see Fig. 3a). Due to the longer acquisition times needed, the sequential oxidation of UO_2 to U_4O_9 before final stabilisation of U_3O_8 was not observed in these experiments. Nonetheless, the main goal of these tests consisted in showing that the temperature at which the UO_2 fluorite structure loses its chemical stability in air can be effectively determined by Raman spectroscopy without the help of any other auxiliary techniques. Indeed, the Stokes/anti-Stokes analysis does give an approximate temperature at which the phase transformations observed with the CIEMAT equipment start to take place in the time frame of the current Raman Laser Heating experiment. Actually, such temperature is close to (560 ± 40) K ((290 ± 40) °C) if we take into account the highest temperature measured before U_3O_8 was detected, in fair agreement with existing literature data.[2]

4. CONCLUSIONS

The development of a reliable method to characterise *in situ* by means of Raman spectroscopy the chemical reactions occurring in a sample, called Raman Laser Heating, has been carried out. The method consists of two steps: 1) producing a local heating on the investigated material by increasing the laser power density, and 2) subsequently acquiring, at a non-altering low laser power density, the corresponding Raman spectrum of the sample in order to analyse its reactivity at the high temperatures induced and under a given atmosphere.

In this work, Raman Laser Heating is especially proposed to evaluate *in situ* the oxidation of actinide dioxides in air. The small size of the laser spot enables analysing such oxidation behaviour with the unique alteration of a minor amount of sample, what constitutes a significant safety advantage when it comes to working with homogeneous radioactive materials.

In order to prove the method's applicability, UO_2 powder has been subjected to Raman Laser Heating, consequently acquiring different Raman spectra corresponding to the sequential oxides (UO_{2+x} and U_4O_9) involved in the air oxidation of UO_2 to U_3O_8, with good reproducibility of the results.

The temperature at which such phase transformations start to occur, in the time frame of the current laser heating experiments, was estimated to be close to (560 ± 40) K ((290 ± 40) °C) in air by performing, with a different set-up, a Stokes/anti-Stokes spectral analysis in similar Raman Laser Heating experiments. This is an important result as it shows how it is indeed possible, using only Raman spectroscopy, to reasonably estimate the temperature at which UO_2 starts to oxidise in air.

The present observations will be useful in the analysis of nuclear fuel and nuclear waste, which can be performed remotely by tailored Raman probes, and, at the same time, *in situ* or *ex situ* on highly radioactive samples.

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