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In situ Raman estimation of irradiation-induced heating of UO_2

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ABSTRACT

We present an *in situ* Raman estimation of the temperature increase of UO_2 pellets induced by cyclotron He^{2+} ionic irradiation in different environments (Ar gas or water): For instance, in the Ar gas environment, the sample is heated to a temperature 150–200 °C (i.e., below the annealing temperature of UO_2 defects). For water, the sample is heated from 30 to 80 °C, just below the range of the studtite/metastudtite and the schoepite/metaschoepite transitions.

1. Introduction

In recent years, in addition of studies on highly active materials (as spent fuels or transuranium actinides [1–3]), ion-beam external irradiation is increasingly used to understand the behavior of UO_2/water interface under alpha radiolysis [4,5] and bulk defect formations [6,7]. However, the local temperature of the sample and its changes due to the irradiation itself has yet to be answered. Among various *in situ* characterization techniques, Raman spectroscopy has received great attention to study UO_2 [1,8–11] and estimation of the local temperature by means of Raman scattering is of major interest due to its local probing capability. Moreover, the micrometric spatial resolution of the Raman setup could give access to the thermal gradient due to inhomogeneity (of the sample) or fluctuations of the irradiation beam. We have already presented the temperature dependence of UO_2 Raman spectra in the temperature range 20–590 °C [12]. Our results showed that the *in situ* wavenumber shift *vs.* temperature due to anharmonicity of a Raman-active vibration mode can be used to measure temperature during irradiation.

In this paper, we then present *in situ* Raman estimation of the temperature increase induced by ionic irradiation, with detailed discussion of the accuracy and interest of the method. The experimental procedure in our study was adopted based on previously published works during the irradiation of UO_2 pellets in aqueous environment [5,13] and under neutral gaseous environment [14]. Although the experimental set-up was quite similar in both cases, the overall objectives were totally different. The study of the UO_2/water interface under irradiation was motivated by the problematic of the long term underground disposal of nuclear waste and the potential degradation of the canister enclosure, thereby allowing water to interact the spent fuel matrix. On the other hand, the UO_2/neutral gas interface was studied with the aim to determine the kinetics of irradiation-induced defect formation in the solid. In both experiments, the irradiation-induced heating was determined to be a critical point. For example during irradiation, a high temperature will favor the annealing of irradiation defects, thus modifies their kinetics of formation [15–17]. Temperature is also one of the critical parameters that define the stability domain of the secondary uranium minerals synthesized during water radiolysis experiments [5,13,18]. It is to be noted that the heating considered in our study is comparatively low to some recent higher temperatures experiments involving actinides [19,20].

2. Experimental and data treatment procedure

In both experiments, sintered UO_2 ceramics (8 mm diameter and 300 μm thick) were used. They samples were also annealed at 1700 °C in reducing Ar/H_2 atmosphere in order to ensure oxygen stoichiometry.

The irradiation cell and the *in situ* Raman installations are both illustrated in Fig. 1(a) and (b) respectively. The same setup and polymer cell were used for both experiments: a first one where the cell was filled with 95% Ar/5% H_2 mixed gas [14] and a second one

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where the cell was filled with deionized water [5,13]. From Fig. 1, one can see that the sample cell is fixed on the ion beamline output of the CEMHTI cyclotron accelerator. The UO_2 pellets were irradiated with a 45 MeV He^{2+} ion beam and with a flux corresponding to 7×10^{15} $He^{2+}{\cdot}m^{-2}$ s^{-1} for the gaseous experiment and 1×10^{15} $He^{2+}{\cdot}m^{-2}$ s^{-1} when the contact medium was deionized water. The temperature dependence of the Raman peaks was recorded by heating a small section of the UO_2 disk in a TS 1500 Linkam optical micro-oven device which allows a very fine temperature regulation as good as ± 1 °C, under 95% Ar/5% H_2 atmosphere [12].

In situ (temperature and irradiation) Raman spectra were collected using a Renishaw RA100 spectrometer equipped with 633 nm line of He–Ne excitation laser and a 1800 grooves/mm holographic grating allowing 4 cm^{-1} spectral resolution and offering a spectral window observation from 130 to 1100 cm^{-1}. Raman parameters, such as the line position (ν_{T2g}) and the linewidth (σ_{T2g}) of the only Raman active mode of UO_2 were obtained using the Renishaw WIRE software from a conventional fitting of the 400–500 cm^{-1} wavenumber range with a Lorentzian function plus a linear background.

In this study, the temperatures were estimated by three ways using the temperature dependence of the Raman T_{2g} peak parameters as previously reported in Ref. [12]. Two temperature estimations were deduced from Equations (1) and (2).

$$T\left(\Delta\nu_{T_{2g}}\right) = 25 - 85\Delta\nu_{T_{2g}} + 119\,\Delta\nu_{T_{2g}}^2 + 28\,\Delta\nu_{T_{2g}}^2 \quad (1)$$

$$T\left(\sigma_{T_{2g}}\right) = -573 + 40\sigma_{T_{2g}} - 0.24\,\sigma_{T_{2g}}^2 \quad (2)$$

A final estimation was carried out by direct graphic comparison of ν_{T2g} with $t\sigma_{T2g}$ for *in situ* under irradiation data sets and *in situ* high temperature measurements (temperature T in °C, line position ν_{T2g} and widths σ_{T2g} in cm^{-1}).

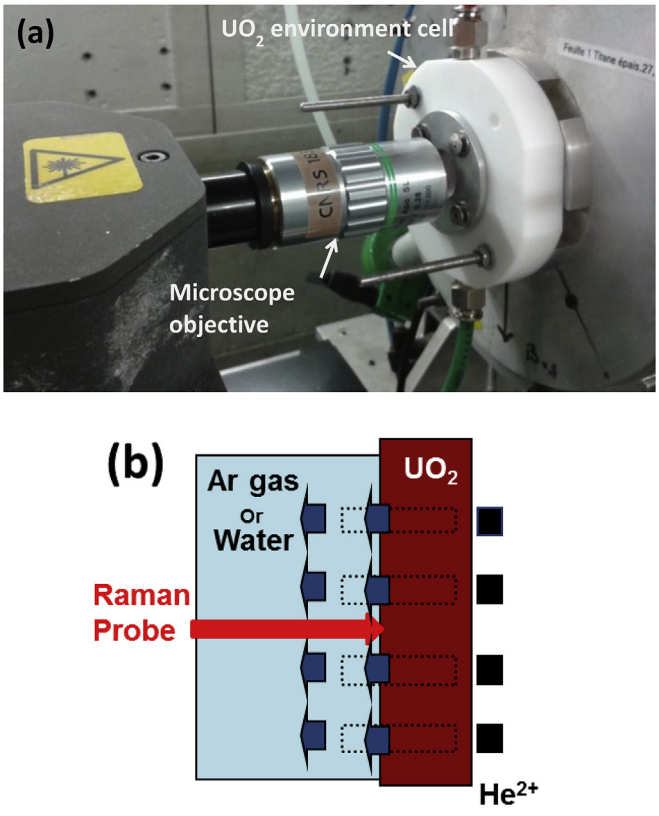

Fig. 1. (a) picture of the irradiation cell and the microscope objective of the Raman probe. (b) Scheme of the *in situ* Raman probing of sample under ionic irradiation.

3. Results and Discussion

Figs. 2 and 3 show the time dependence of ν_{T2g} (t) and σ_{T2g} (t) for the gaseous and water experiments respectively. The grey areas indicate the acquired Raman data during the irradiation conditions, while the white areas correspond to the data set when the measurement was carried out without the He^{2+} ion beam.

Both ν_{T2g}(t) and σ_{T2g}(t) exhibit a strong noise and maximum values were fixed visually by taking account of small overshoots and outliers values. The dashed lines of Figs. 2 and 3 picture these maximum and minimum values. For the water radiolysis experiment, the calculated average value for the $\Delta\nu_{T2g}$(T), i.e., the difference between the ν_{T2g}(T) and the $\nu_{T2g}(T_{room})$ at room temperature, and σ_{T2g} due to the heating are $\Delta\nu_{T2g}$ = - 0.1 cm^{-1} and σ_{T2g} = 18.3 cm^{-1} respectively. On the other hand, the UO_2/Ar interface shows that the values of $\Delta\nu_{T2g}$ and σ_{T2g} are −1 cm^{-1} and 21 cm^{-1} respectively. The corresponding temperatures with the T($\Delta\nu_{T2g}$) and T(σ_{T2g}) relations obtained in Ref. [12] and calculated using Equations (1) and (2) are noted on the right side of Figs. 2 and 3 and also summarized in Table 1. The maximum temperature was estimated from the axis with less data dispersion and is illustrated as the dashed lines in Fig. 4. The results give the values of T_{gas} = 190 °C and T_{water} = 50 °C that are also reported in Table 1. The following section is devoted to discuss the different values for the estimated temperatures induced by the irradiation (160, 190, 200 °C for the gas experiment and 35, 50, 80 °C for the water experiment).

From the *in situ* high temperature Raman spectra of UO_2 [12], we know that the relative Raman frequency shift $\Delta\nu_{T2g}$ = ν_{T2g}(T) - ν_{T2g}(room T) and the width σ_{T2g} of the T_{2g} Raman peak are respectively decreased and increased upon heating. Besides, these spectral parameters were also shown being partially permanently modified by the exposure to ionic irradiation [14]. In order to discriminate the irradiation effect on the spectral parameters $\Delta\nu_{T2g}$ and σ_{T2g} from the temperature effect on them, one should take into account that the irradiation-induced damage effect is a non-reversible effect that can be probed with *post-mortem* experiments (provided irradiation-induced heating does not induce annealing effects) whereas temperature-induced changes are

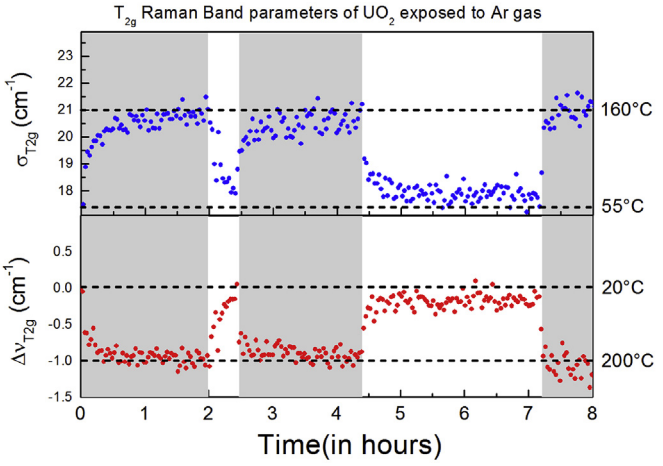

Fig. 2. Time dependence of $\Delta\nu_{T2g}$ and σ_{T2g} parameters during irradiation of a UO_2 pellet in contact with Ar gas (see Ref. [14]). Irradiation time is back-grey and the reported temperature comes from Equations (1) and (2).