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Charged defects during alpha-irradiation of actinide oxides as revealed by Raman and luminescence spectroscopy

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ABSTRACT

We have recently evidenced an original Raman signature of alpha irradiation-induced defects in UO_2. In this study, we aim to determine whether the same signature also exists in different actinide oxides, namely ThO_2 and PuO_2. Sintered UO_2 and ThO_2 were initially irradiated with 21 MeV He^{2+} ions using a cyclotron device and were subjected to an *in situ* luminescence experiment followed by Raman analysis. In addition, a PuO_2 sample which had accumulated self-irradiation damage due to alpha particles was investigated only by Raman measurement. Results obtained for the initially white ThO_2 showed that a blue color appeared in the irradiated areas as well as luminescence signals during irradiation. However, Raman spectroscopic analysis showed the absence of Raman signature in ThO_2. In contrast, the irradiated UO_2 and PuO_2 confirmed the presence of the Raman signature but no luminescence peaks were observed. The proposed mechanism involves electronic defects in ThO_2, while a coupling between electronic defects and phonons is required to explain the Raman spectra for UO_2 and PuO_2.

1. Introduction

Accurate determination of nuclear fuel behaviors in normal or accidental condition is a challenge for the nuclear industry in order to ensure its safety and profitability. Irradiation damages have a direct impact on the physical properties of the nuclear fuels and several theoretical works are currently in progress aiming to determine the stable point defect in UO_2. Unfortunately, limited experimental data is available to characterize irradiation defects in nuclear fuels. X-Ray diffraction and Transmission Electron Microscope evidenced changes in the crystalline structure and grain microstructure during irradiation [1,2]; however these methods are not well suited to evidence point defects. Recently [3] evidenced a specific signature of irradiation in UO_2 using Raman spectroscopy. This signal corresponds to three additional peaks in the Raman spectrum of UO_2 implanted with alpha ions and can be related to a single defect that is annealed between 300 °C and 525 °C [4]. According to [5] its creation kinetics can be modelled by a single impact model and has previously been used to describe UO_2 cell parameter behavior under irradiation. These results observed by Raman spectroscopy has characteristics similar to irradiation-induced point defects, and therefore deserved an in-depth characterization and understanding.

A striking feature of the Raman defect arises from its creation process. According to SRIM code, a 25 MeV helium ion beam will primarily lose its energy through electronic stopping. However, the electronic energy due to the alpha ions ($dE/dx = 1$ keV/nm) is much weaker than the value reported in literature for creation of tracks by swift heavy ions [6]. In that range of deposited energy, only self-trapped excitons or colored defects could be formed [7]. To date the existence of such defect types has not been reported about irradiated UO_2.

This paper is devoted to understand the behavior of three actinide oxides namely UO_2, ThO_2 and PuO_2 since they all share the same crystallographic structure, with similar mass, density and number of electrons. The study aims to look at the existence of electronic processes in these oxides. Moreover the energy deposited profile in all these compounds, as determined by SRIM, shows same trend and this suggests that they should have similar behavior under irradiation.

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2. Experimental procedure

2.1. Samples

Sintered UO_2 and ThO_2 samples were prepared at CEA-Cadarache and ICSM, respectively. UO_2 discs were heat treated at 1700 °C under dry Ar/H_2 while ThO_2 was sintered at 1600 °C in air. The discs were all mirror-polished at one side and then annealed at 1000 °C to maintain stoichiometry and also remove polishing damages. Prior to irradiation, both UO_2 and ThO_2 pellets were analyzed using the Scanning Electron Microscope and Raman Spectroscopy. In both cases, no traces of fuel oxidation were observed, as it will be further detailed in Section 3.3.1.

In this work, the pellets were sectioned into two-half discs along their cylindrical axis as it allows to correlate the penetration profile of the ions along the depth of the samples with simulated data as described in [3]. The irradiation was performed at the Cyclotron facility, CEMHTI Orléans (France) and it was possible to carry out both *in situ* (Ion-Beam Induced Luminescence) and *ex situ* (Visual and Raman) experiments.

A PuO_2 sample was initially prepared at CEA-Cadarache and heat treated at 1700 °C under reducing environment for 2 h back in 2011. The pellet showed a high activity due to the presence of alpha emitters. To consider the effect of alpha particles, the PuO_2 was left to decay for 2.5 years during which its activity was reduced by 2.1×10^9 Bq. The auto-irradiated pellet was later characterized with Raman spectroscopy in 2013.

2.2. Irradiation

The UO_2 and ThO_2 half-disks were all irradiated with 21 MeV He^{2+} during 2 h and an ion flow of 50 nA using the cyclotron device. The energy chosen was able to deliver more electronic energy ($(dE/dx) = 132$ keV/μm) near the surface of the pellets. All irradiations were carried out at room temperature and under vacuum so as to prevent any risk of pellet oxidation.

2.3. Ion-Beam Induced Luminescence experiment (in situ)

The luminescence set-up used to monitor the behavior of UO_2 and ThO_2 during irradiation consisted of an optical set-up of a pyrometer probe implemented on the CEMHTI cyclotron beam line and positioned in the direction of the pellet's surface exposed to the irradiation beam. An optical fiber coming from the pyrometer probe-head was connected to a one-grating monochromator (SR 163 Shamrock Andor) and an ICCD multichannel detector (Andor iStar DH720) all located in a safety room 20 m away from the irradiation cell, by means of optical fibers and electrical cables.

2.4. Raman measurement (ex situ)

A Renishaw RA-100 Raman Analyzer was used to characterize fuel oxides before and after irradiation. A 633 nm He–Ne was initially employed and each Raman spectrum was acquired through an acquisition time of 40 s for a wavelength ranging from 300 cm^{-1} to 700 cm^{-1}. A second step consisted of analyzing the irradiated pellets using a 532 nm green laser so as to confirm the presence of Raman signals.

A similar procedure was applied for PuO_2; however with a different experimental procedure. This set-up variance was necessary since the sample was contained within a glove box to prevent radiological contamination. Hence the Raman head was placed outside the box, with the laser focused onto the sample passing through the glass of the glove compartment (Mitutoyo x20 objective, 30 mm front distance).

3. Results

3.1. Ion-Beam Induced Luminescence

The luminescence spectrum of ThO_2 was recorded for a wavelength ranging from 200 nm to 800 nm during irradiation as shown in Fig. 1. Before irradiation ($t = 0$ min), the ThO_2 sample emits no luminescence signals. The spectrum is largely modified given the number of peaks appearing during the initial stage of the He^{2+} beam. It can be seen that more emission occurs between 300 nm and 620 nm which could be related to the formation of electronic defects in the material as discussed by [8].

However under the same irradiation conditions, no luminescence peaks were observed in UO_2 as its spectrum remained unchanged even when the ion flow was increased from 50 nA up to 200 nA. This result provides evidence that a different defect mechanism is involved in UO_2 compared to ThO_2 even if they are irradiated under the same conditions.

3.2. Visual inspection

The UO_2 and ThO_2 samples were both visually compared. Although UO_2 exhibited no significant change in its physical appearance, the sections of the initially white ThO_2 exposed to the irradiation beam turned into a deep blue color (Fig. 2). The coloration of ThO_2 has previously been observed [9–12,13] reported that it take its origin from colored defects with swallow energy which can be annealed out at high temperature.

3.3. Raman spectroscopy

3.3.1. Before irradiation

As mentioned, the 633 nm was initially used to obtain the Raman spectra of the fresh pellets. UO_2 and ThO_2 share the same fluorite structure with the Fm3m space group. According to their phonon dispersion curves [14,15], they have a single Raman active mode

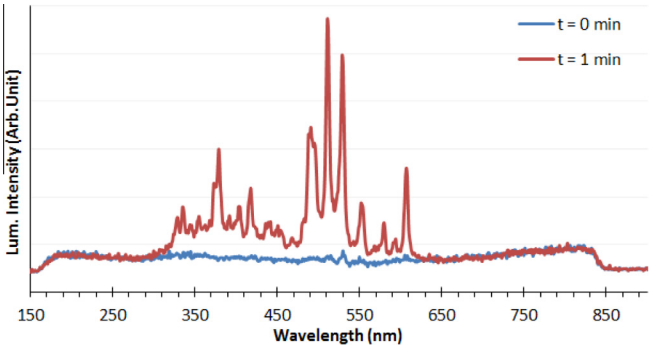

Fig. 1. Luminescence spectrum of ThO_2 during 21 MeV He^{2+} and 50 nA ion flow [Color online].

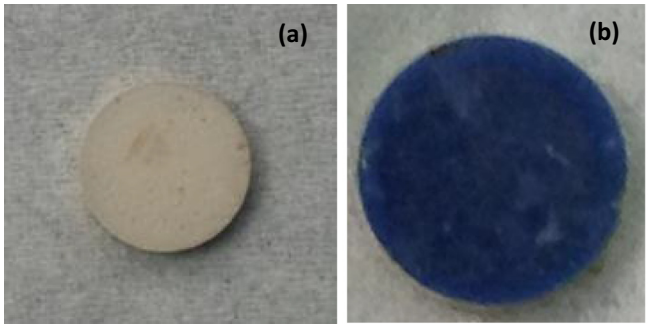

Fig. 2. ThO_2 pellet (a) before and (b) after irradiation respectively [Color online].