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Laser-Induced Annealing of Aged PuO_2

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Abstract
Plutonium dioxide (PuO_2) is an important compound used in nuclear fuel, irradiation targets, and heat sources. As such, improved understanding of its structural and spectroscopic properties has numerous applications. Alpha particle-induced damage of a PuO_2 crystal lattice modifies several properties of its Raman spectrum, including band intensities, positions, and widths. The decay also induces growth of new bands and creates electron-trapped defects with luminescent properties. Herein, we show for the first time that laser-induced heating can reverse damage to an aged and damaged PuO_2 lattice. Using automated instrumentation to heat a single 6-10 μm spot to temperatures above 1300°C, we show that laser-induced annealing of aged PuO_2 results in restoration of T_{2g} band intensity with a concomitant decrease in defect band intensity; a result that indicates laser annealing can be used to reverse age-damage in PuO_2. This laser annealing approach permitted *in situ* observation of temperature-dependent Raman spectral changes, thereby providing insight into the thermodynamics of structural alterations in a radiolytically damaged PuO_2.

Keywords: PuO_2, alpha decay, lattice damage, laser-induced annealing, nuclear forensics

Introduction

In nuclear forensics, determination of physical and chemical characteristics, process history, and age of interdicted nuclear material is vital in determining material provenance.[1] Radioactive decay in alpha particle-emitting elements like plutonium, results in crystal lattice damage, the extent of which can be used to determine the time elapsed since the material was last annealed/calcined to a pristine state.[2]

Specific damage mechanisms in alpha-emitting materials include formation of Frenkel defects, cation interstitials, electron-hole pairs, and charge defects.[3] Significant lattice damage can change the lattice parameter ($\Delta a/a$) and can be measured by X-ray diffraction (XRD), as has been shown in UO_2, PuO_2, and mixed Pu/U oxide materials.[4,5] Raman spectroscopy can also be used to detect lattice damage by measuring changes in the intensity, position, and full-width at half-maximum of spectral bands.[2]

The Raman spectrum of PuO_2 exhibits multiple bands between 350-1300 cm^{-1}; the T_{2g} Raman mode (~479 cm^{-1}), the 2LO2 overtone (1150 cm^{-1}), and a band corresponding to an electronic transition (1047 cm^{-1}).[6] If the material is aged, defects bands are observed at 580, 625, and 650 cm^{-1}.[7] Also observable in the spectrum of aged PuO_2 is a large feature attributable to plutonium luminescence from electron-trapped defects.[6,8]

Recently, thermal annealing of defects in aged PuO_2 was observed using Raman measurements of samples heated up to 1000°C. The intensity of defect bands in the Raman spectrum was shown to decrease above 600°C; a result attributed to repair of Frenkel defects.[9] In this example, bulk powders were heated treated in air, resulting in a limited number of analyzed temperatures.

Herein, we describe an automated stepwise laser method to induce annealing of aged PuO_2. Because annealing was performed with a laser, *in situ* Raman measurements were performed immediately following heating. This technique permitted extraction of spectral signatures related to the age of the material and the approximate temperatures at which the material's specific defects are annealed. In contrast to previous aging studies, this is the first time that high-resolution stepwise laser-induced annealing has been combined with Raman spectroscopy to study PuO_2 aging/annealing. This

innovative approach to automated high-resolution Raman spectroscopy allowed for the execution of multi-day experiments involving numerous heating steps and spectral acquisition cycles.

Materials and Methods

Powder PuO_2 used in these experiments was last calcined at 1000°C in air 5 years prior to the start of our spectroscopy experiments. Therefore, the material had undergone 5 years of radiolytic damage when we first measured it.[6] Non-stoichiometric PuO_2 compositions are possible due to water absorption[8, 10]; however, the high calcination temperature for our material, its storage under sealed double-containment, and IR evidence showing little water, leads to the conclusion that our sample stoichiometry was very close to PuO_2. High ^{240}Pu content (98% ^{240}Pu) PuO_2 was used to accelerate alpha-decay relative to high ^{239}Pu content PuO_2. The loose PuO_2 powder was adhered to carbon tape, and a spot approximately 6 – 10 μm was analyzed (see Fig. S1 for a representative micrograph of this powder). All data presented herein relate to a single analysis site on the PuO_2;analyzes of different sites in the same material found the measurements to be reproducible. Analysis by Raman was conducted in ambient air with approximately 25% relative humidity. Additional details of material synthesis and the Raman microspectroscopy system are described elsewhere.[2,6-7, 11] Briefly, Raman spectra were measured with a LabRAM HR800 UV, equipped with iDus detector (DU416A-LDC-DD). Scripts written in Python code were used with LabSpec 5.78 software to control the spectrometer, detector, and laser power at the sample. The laser power at the sample was controlled with a ½ waveplate in combination with a polarizer. For all spectra, band intensity data was a calculated average of the intensity at the band maximum and ± 1 cm^{-1} around the maximum.

An initial Raman spectrum of PuO_2 was acquired with a 514 nm laser operating at 0.25 mW. The laser power was then increased to 0.5 mW for ten minutes to induce heating/annealing while the Stokes (S) and anti-Stokes (AS) intensities of the T_{2g} band were acquired to allow calculation of temperature. Prior to Raman spectral acquisition, the laser was turned off and the sample was allowed to cool to room temperature (as verified by the ratio of the T_{2g} S and AS bands). The Raman spectrum was then acquired with a laser power of 0.25 mW. This process was repeated on the same sample spot by increasing the annealing laser power in 0.5 mW increments until 24 mW was reached.

Temperatures calculated from the intensity of the S and AS bands were found to be linear with laser power up to ~ 1125°C (19 mW) (see Fig. S2 and S3). Linear extrapolation was used to estimate higher annealing temperatures and temperature precision may be lower at temperatures above ~1125°C. Raman thermometry was tested with a Linkam stage up to 500°C with a silicon standard and the calculated temperature from the intensity of the S and AS bands of the standard were within 5°C of the temperature measured with a thermocouple. Except for comparisons of band properties (FWHM) between material calcined in a furnace and laser-annealing of the material at a given temperature, it was impossible at this time to establish accuracy from estimated temperatures using the laser-induced annealing methodology. Therefore, temperature precision, instead of temperature accuracy is used in this manuscript with our PuO_2 measurements. Based on linear fitting techniques described in the supporting information, we nominally ascribe a temperature precision of ±15 °C for measurements acquired up to ~ 1125°C. See supporting information for a more detailed discussion of how the sample temperature and precision was derived.

Results and Discussion

Fig. 1 shows the spectral series for the laser-induced annealing experiments. The luminescence background in the spectra was removed to improve visualization of the intensity of the Raman bands. A detailed discussion of the T_{2g} band intensity and position is presented elsewhere.[6] Starting around 200°C (3.5 mW), the T_{2g} intensity begins to increase with temperature. This increase is apparent in Fig. 2 where we plot band intensity versus laser power and calculated temperature. The intensity of the T_{2g} band continues to increase at all temperatures measured. The rate of intensity increase is greatest at higher temperatures. At temperatures above ~1300°C, the rate of the T_{2g} intensity increase slowed. Importantly, under intense heat, the sample holder began to deform causing the PuO_2 sample to move out of focus. Thus, it is unclear if slowing of the T_{2g} intensity increase was due to sample movement or the system approaching a fully annealed state. The electronic band (1047 cm^{-1}) was found to increase proportionally to the T_{2g} band.

Within the T_{2g} band intensity increase is an interesting hump-like feature around ~730 – 912°C where the intensity is further modified. This behavior coincides with a reduction in intensity of the 580 and 650 cm^{-1} defect bands as well as an increase in the 625 cm^{-1} band. These data suggest there may be distinct temperature ranges where annealing of specific defects occur. These ranges may correlate with changes in the T_{2g} band intensity; however, additional experiments would be needed to build a quantitative model around these observations.

To better understand the laser annealing mechanism, we also analyzed intensity changes of the three defect bands. The defect bands have significant scatter and are much lower in intensity than the T_{2g} band but still exhibit clear changes in intensities with increasing temperature (see Fig. 2 and Fig. S4). Similar to the T_{2g} band, additional experiments would be needed to build a quantitative model around our observations; nonetheless, some general discussion of these bands is provided below. For a comparison of defect bands in UO2 and PuO2, see Mohun et al.[12]

The 650 cm^{-1} defect band exhibited a sharp decrease in intensity around 486°C, but the decrease ceased around 790°C. Based on the low temperature where this band decreases in intensity and previous studies of UO_2, we tentatively ascribe the origin of the 650 cm^{-1} band to Frenkel pairs involving displaced oxygen atoms that are annealed at relatively low temperatures.[4]

Changes in the intensity of the 625 cm^{-1} band were more complex with the band increasing in intensity between ~ 638°C - 852°C and then decreasing in intensity at temperatures above ~ 852°C. The 625 cm^{-1} band may be interrelated to the 650 cm^{-1} band since the 650 cm^{-1} band decreases sharply near the same temperature that the 625 cm^{-1} band increases sharply. At ~685°C the intensities of the 650 and the 625 cm^{-1} Raman bands are equivalent.

The 580 cm^{-1} band exhibited a sharp decrease in intensity around 730°C and continued to decrease in intensity at all higher temperatures measured. Because the defects which resulted in the 580 and 625 cm^{-1} Raman band continued decreasing at such high temperatures, we tentatively ascribe the origin of these bands to multiple defects, including α-helium in vacancies, and cationic Frenkel pairs.[4]

Overall, removal of defects in PuO_2 occurs at slightly higher temperatures than annealing of defects in other actinide and mixed actinide oxide materials;[4,5] a result that is consistent with recent results by Harker et al.[9] PuO_2 typically undergoes an increase in density and concomitant decrease in specific

surface area with increased bulk temperature.[13] It is unclear if similar changes occurred during laser-annealing experiments; however, if a large morphological shift occurred, the temperature v. laser power plot Fig. S3) would be expected to deviate from linearity, which was not observed.

Analysis of higher energy (> 2000 cm^{-1}) electronic transitions in PuO_2 were omitted from this manuscript for brevity; however, analysis of the evolution of these transitions with increasing temperature is described in detailed elsewhere.[14] In principal, our laser-annealing technique should be capable of studying these higher energy transitions in future work.

Summary

An automated method for laser-annealing radiolytically-damaged PuO_2 has been disclosed. This method enabled *in situ* observation of changes in the PuO_2 Raman spectral bands over a large range of temperatures. Laser-annealing caused an increase in the T_{2g} band intensity with concurrent decrease in intensity of the Raman bands which originate from defects in the PuO_2 material. These data provide unique thermodynamic information which could be used to guide future theoretical calculations on radiolytically-damaged PuO_2. Efforts are currently underway to use this laser-based annealing technique to quantify thermochemical parameters of PuO_2 lattice defects.

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