Raman Spectroscopy: A Tool to Investigate Alpha Decay Damage in a PuO_2 Crystal Lattice and Determining Sample Age Since Calcination

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Abstract

Raman microspectroscopy can be used to measure local physical properties of materials, such as the lattice parameter. Alpha decay induced lattice damage of plutonium dioxide (PuO_2) results in the growth of new bands and broadening of the T_{2g} band. A relationship between the change in the lattice parameter and storage time has been established in the literature using X-ray diffraction (XRD). Our measured time dependent Raman spectra of PuO_2 particulates matches the XRD results. This new Raman spectroscopic technique can provide dating information on the time elapsed since the last calcination of PuO_2 using a single >5 µm particulate in contrast to 50 mg of 10-50 µm particles required by XRD.

Keywords: plutonium dioxide, alpha decay, lattice damage, laser annealing, nuclear forensics

Introduction

PuO_2 belongs to the fluorite structure group and is described as a face centered cubic sublattice. Group theory analysis of PuO_2 results in one Raman active mode, the T_{2g} mode, located near 480 cm^{-1} (Figure 1) and two infrared active modes. New Raman bands measured in the PuO_2 Raman spectrum are indicative of broken symmetry within the material, meaning previously forbidden transitions have become allowed Raman transitions. An alternate explanation of the new Raman bands is due to the creation of cation and anion Frenkel pairs via alpha decay, which leads to structural changes within the crystal.

PuO_2 properties are sensitive to initial production conditions and crystal lattice damage via self-irradiation. The degree of crystallinity is slowly altered over time by plutonium alpha decay. The energetic alpha particles and recoiling nuclei create significant, detectable defects and vacancies in the crystal structure.[1] Raman microspectroscopy can detect these changes over time by interrogating PuO_2 localized physical properties. While crystallographic damage in PuO_2 materials is well-known,[1-3] a recent study[3] shows how these crystallographic changes manifest in two additional Raman-active vibrational bands in the “Aging” region of Figure 1 (580 cm^{-1} (1LO2 mode) and 650 cm^{-1}).[3-5] We used Raman microspectroscopy to measure the intensity and full-width half-maxima of PuO_2 vibrational bands over time to determine the time elapsed since the final processing step of calcination/annealing.

Materials and Methods

Plutonium (^{240}Pu) material was synthesized within a once-through, multiple HEPA filtered, negative pressure glovebox. The plutonium material used plutonium holdings at Savannah River National Laboratory. The plutonium material was dissolved in nitric acid (HNO_3) and purified using an anion exchange (Relliex HPQ) followed by elution in 0.35 M HNO_3. PuO_2 was produced by calcining the eluted solution in air at 1000°C for two hours. The prepared sample was stored in a double wall containment cell[6] under ambient conditions.

Details of the Raman microspectroscopy system have been described previously.[6,7] Briefly, Raman spectra of PuO_2 were measured with a modified commercial system (LabRAM HR800 UV, Horiba Jobin-Yvon) along with a Newton EMCCD (Andor 970N-UVB) detector, accurate within 0.5 cm^{-1}. LabSpec 5.78 software controlled the spectrometer and detector. A 514 nm laser line from an Ar ion laser measured the PuO_2 Raman spectra with powers <5mW at the sample. Five different crystalline particle aggregates (150-300 µm diameter, composed of nm size crystals) within the sample were annealed with 50 mW of power for ten minutes with a 514 nm excitation laser using a 50x microscope objective to anneal an area of approximately 6 μm in diameter at the particle aggregate surface. Neutral density filters controlled the laser intensity at the sample.

Results and Discussion

Figure 1 shows Raman spectra of the PuO_2 sample in the spectral region of 250 to 750 cm^{-1} at different times over more than two years. The broadening of the band corresponding to the T_{2g} vibrational mode and growth of the two peaks corresponding to (symmetry-breaking) vibrational bands at higher wavenumbers (labeled 'Aging'), are changes in Raman spectral features attributed to the growth of alpha-induced crystalline defects in the particle since synthesis of the material.

The number density of damage sites depends on elapsed time, but also on the inventory of alpha-emitters within the material.[8-10] Consistent with the damage in previously studied nuclear materials, XRD measurements of the PuO_2 lattice parameter show an increase as a function of storage time due to self-radiation damage from alpha-decay of plutonium.[8-10] The following equation represents the established relationship:[2]

$$\frac{\Delta a}{a_0} = A(1 - e^{-B\tau t}) \tag{1}$$

where a_0 is the lattice parameter after preparation, Δa is the change in lattice parameter via self-radiation, A and B are constants, τ is the decay constant of the actinide isotope and t is storage time. The established relationship is dependent on three different constants: τ (decay constant associated with the alpha-emitting isotope(s) present), A (maximum change in lattice parameter), and B (a measure of the rate of change of the lattice parameter, kinetic constant). A and B are intrinsic to the PuO_2 lattice and will be the same for different isotopes of plutonium. Because τ is different for each plutonium isotope, using the same τ to plot the exponential regressions for each isotope places all the regressions onto the same time scale, allowing for direct comparisons. Figure 2 plots the exponential regressions of the change in the XRD lattice parameter as a function of storage time for $^{239}PuO_2$, $^{238}PuO_2$, and a mixture of $^{239}PuO_2$, $^{238}PuO_2$ and $^{241}AmO_2$. Since the available XRD data[2] was from different plutonium isotopes, the τ for ^{240}Pu was used to plot the exponential regressions on a common time scale.

The PuO_2 particulate aggregates were analyzed for 16 months by measuring laser-annealed aggregates (clock reset) and aged aggregates. The measurements were conducted monthly to determine the growth rate of bands related to crystal lattice damage. $^{240}PuO_2$ has a specific alpha decay rate 3.6 times faster than $^{239}PuO_2$ and was selected to accelerate the rate of alpha induced damage. The τ for $^{240}PuO_2$ was used to plot the exponential regressions of the XRD results[2] to be on the same time scale as the Raman results. The Raman results from the measured full-width at half-maximum (FWHM) of the T_{2g} band as a function of storage time match the lattice parameter change measured with XRD (Figure 2a). The ratio of the fit areas of the aging and T_{2g} bands with respect to storage time also matches the XRD results (Figure 2b). These Raman results indicate an exponential relationship with storage time, analogous to the XRD literature[2] results and our results are also consistent with alpha-recoil track studies performed on other nuclear materials[8-10].

Conclusions

Analysis of these Raman spectral features accurately measures the time since a PuO_2 sample was calcined, based on the growth of alpha-induced crystalline defects. This method of age-dating produces results in agreement with XRD measurements when applied to bulk lattice analysis. This Raman spectroscopy method can be used to measure self-radiation damage from alpha-decay of plutonium that matches literature XRD results[2].

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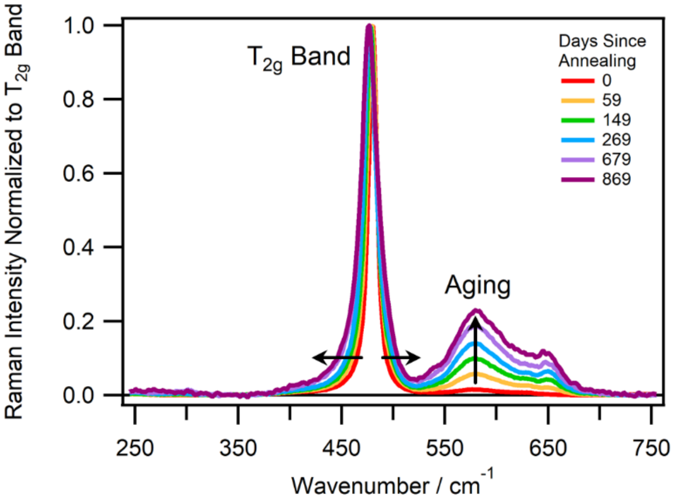

Figure 1: Normalized Raman spectra of PuO_2 after annealing – thereby removing prior alpha-induced defects – and aging under ambient conditions for over two years.

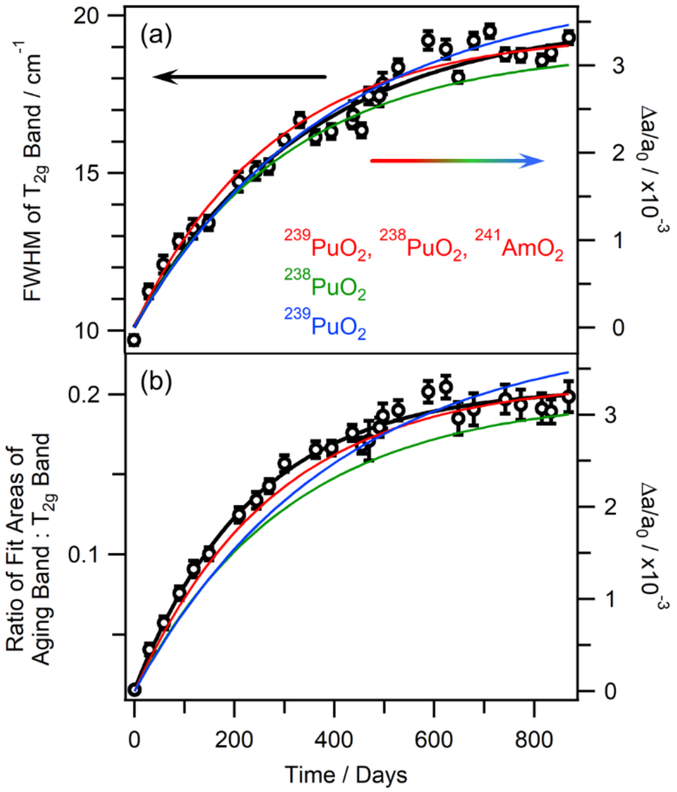

Figure 2: Relative changes in Raman spectral features as a function of time. Full-width-half-maximum of band corresponding to T_{2g} vibrational mode (a) and ratio of aging band to T_{2g} peak (b). The error bars are estimated uncertainties at 95% confidence and colored curves correspond to extrapolations based on prior XRD measurements[2].