



**NATIVE DEFECT CHARACTERIZATION OF SINGLE CRYSTAL UO_2 PRE-
AND POST-NEUTRON IRRADIATION**

THESIS

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AFIT-ENP-MS-18-M-084

**DEPARTMENT OF THE AIR FORCE
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Abstract

Synthetic single crystal uranium dioxide (UO_2) samples were studied using photoluminescence (PL) to characterize the surface defects present following growth. X-ray Fluorescence (XRF) and gamma ray spectroscopy measurements were collected to help identify any impurities present in the sample. PL measurements were made using a *Kimmon Koha Co., LTD.* IK series helium-cadmium (HeCd) 325 nm laser with an energy range of 5 mW/10 mV, in a 10^{-6} Torr vacuum, and at 10K. Data was collected through a *Products for Research Inc. PHOTOCOOLTM* series photomultiplier tube (PMT) attached to a *Horiba Scientific Inc. SPEX 1250 M* monochromator and analyzed with *SynerJYTM*.

Both the emission of U^{4+} in UO_2 from $5f^16d^1 \rightarrow 5f^2$ transitions and uranyl emission from surface oxidation was detected. Five $5f^16d^1 \rightarrow 5f^2$ transitions were assigned to peaks at 3.41 ± 0.02 , 3.17 ± 0.02 , 3.00 ± 0.02 , 2.82 ± 0.02 , and 2.61 ± 0.01 eV. Six near band edge (NBE) defects were detected and their phonon replicas identified. The uranyl symmetric ($797.6 \pm 6.1 \text{ cm}^{-1}$), antisymmetric ($850.8 \pm 7.7 \text{ cm}^{-1}$), bending ($171.4 \pm 4.4 / 205.3 \pm 0.9 / 254.6 \pm 1.9 \text{ cm}^{-1}$), and inherent internal defect ($50.9 \pm 6.6 \text{ cm}^{-1}$) vibrational frequencies are identified for the first time in single crystal UO_2 and in good agreement with other uranyl compounds in literature.

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Steven M. Hoak

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NATIVE DEFECT CHARACTERIZATION OF SINGLE CRYSTAL UO_2 PRE- AND POST-NEUTRON IRRADIATION

I. Introduction

1.1 General Issue

Interception of illicitly trafficked nuclear material is a national security priority. The capability to detect the presence of nuclear/radiological material through emitted radiation is fundamental to countering modern terrorism. Much of the detection efforts for national security, both at home and abroad, have relied on ^3He -based neutron detection. ^3He , the product of tritium decay [^3H ($t_{1/2} = 12.3 \text{ y}$) $\rightarrow \text{He} + \beta^-$], was in abundance for many years thanks to active U.S. and Soviet thermonuclear weapons programs. Since both nations have ceased new production and reduced existing stockpiles, the ^3H supply, and subsequently the ^3He supply, has dwindled [1]. New fields of science, medicine, and new commercial technologies have also pushed the ^3He demand further beyond supply. Starting in 2008, the Department of Energy (DOE) began to strictly regulate the U.S. supply giving priority to the Department of Homeland Security (DHS), other governmental agencies, and U.S. scientific and commercial interests [2]. As a result, the interest in alternatives that can match the detection performance of ^3He -based detectors has sharply increased.

Some current alternatives that are in development or in use are BF_3 -filled and boron-lined proportional counters, glass fibers loaded with ^6Li , doped scintillators, and neutron-capture gamma-ray detectors [3]. A novel technology currently being explored is

crystalline actinide-based neutron-detecting semiconductors. Using fissionable elements as the solid state and electronic medium can potentially produce smaller semiconducting detectors, thus lowering power requirements while improving signal-to-noise ratio and resolution over existing alternatives. Recent research at the Air Force Research Laboratory (AFRL) has produced single crystal uranium dioxide (UO_2) crystals via a hydrothermal growth process. Published relevant research into single crystal UO_2 material characterization is limited compared to the substantial amount of literature available on other forms of UO_2 . If the end goal is to engineer a credible single crystal UO_2 -based neutron detector, the fundamental material properties of the crystals must first be understood. However, before the material properties can be characterized, any elemental and structural impurities that exist within the crystal because of the growth process must be first identified. This research sets out to determine some of these properties in an effort to help guide and facilitate future investigations into other material characteristics necessary to produce a solid-state detection device.

1.2 Problem Statement

Since the hydrothermal growth of single crystal UO_2 remains novel, there is little relevant research into the material characterization of these higher ordered crystal structures outside of ongoing research at the Air Force Institute of Technology (AFIT) and AFRL. Specifically, little is known about what impurities exist in the crystals following growth, and nothing is known of the effects of fission fragment formation on a single crystal. Therefore, how these crystals respond to radiation and how to improve the growth process remains undetermined.

1.3 Research Objectives

The objective of this research is to investigate the elemental and structural defects present in hydrothermally grown single crystal UO_2 prior to and following neutron irradiation using cathodoluminescence (CL) and photoluminescence (PL) spectroscopy. Specifically, the primary objective is to measure the presence and identify native defects in the single crystal UO_2 pre-irradiation. Additionally, following irradiation by neutrons, measure and analyze fission-induced changes to the structural characteristics.

1.4 Research Hypotheses

1. Native defects of hydrothermally grown single crystalline UO_2 are present and can be detected through CL and PL.
2. Neutron-induced fission introduces defects that can be detected through CL and PL.

1.5 Initial Research Plan

Crystal samples will undergo x-ray fluorescence (XRF) and gamma spectroscopy measurements with an HPGe gamma-ray detector in order to gain an initial perspective on the presence and quantity of ^{238}U decay products and foreign impurities present in the sample. Next, defect detection and characterization will be performed through CL and PL prior to neutron irradiation in order to determine the presence of native defects, their energy levels, and their depth in the crystal samples. Samples will then be neutron

irradiated with an Adelphi DD109 deuterium-deuterium (DD) neutron generator.

Following the irradiation, gamma-ray spectroscopy, CL, and PL will be performed again to confirm the addition of defects, their energy levels, depths, and impurity species in the crystal samples.

1.6 Sponsorship

The research contained in this document is sponsored and funded by the (formerly) Domestic Nuclear Detection Office (DNDO). The information contained within this document provides a record of the work accomplished in support of their mission.

II. Theoretical Background

2.1 Chapter Overview

This chapter highlights the relevant theory as it pertains to defect characterization in UO_2 pre- and post-irradiation. It is broken down into six major sections. The first highlights the important past work on this very subject. Next, considerable time is spent laying the foundation of the important physical properties of UO_2 . Without a firm understanding of the structural, bonding, and electronic properties, no analysis of potential defects can be completed as there would be no way to intelligently discern the presence of intrinsic defects. This will be followed with an overview of semiconductor point defects relevant to UO_2 , the hydrothermal growth process of UO_2 used in this experiment, and subsequent higher oxidation states of UO_2 . The chapter closes with an in-depth look into the phenomenon known as luminescence and its relevance to UO_2 .

2.2 Previous Studies

Since UO_2 is the primary fuel for most modern nuclear reactors, its material properties have been extensively studied. Though UO_2 has been discussed as a potential semiconductor since 1958 [4], Meek *et al.*'s report on actinide oxide electronic and optical similarities with, and advantages over, conventional semiconductors helped initiate the current interest [5]. Recent studies into hydrothermal growth [6] and luminescence of single crystal thorium dioxide (ThO_2) at AFIT [7][8] have provided

valuable crystal property information to build upon. However, research in single crystal UO_2 is still limited.

Research into single crystal UO_2 luminescence by way of CL is also limited. CL performed on single crystal $\text{U}_{0.04}\text{Th}_{0.96}\text{O}_2$ produced two emission peaks at approximately 3250 Å and 5200 Å. However, no explanation as to the source was provided [9]. Another study on time-variable crystal oxidation found an emission peak at 4700 Å [10]. This peak's source, as were emission peaks in similar previous ThO_2 CL studies [11] [7], was attributed to an F-center excitation.

To the best of this author's knowledge, there is no readily available research into photoluminescence (PL) of single crystal UO_2 . However, ThO_2 has been studied with PL. Harvey *et al.* showed through PL that wide varieties of impurities, probably transition metals, were incorporated in ThO_2 crystals grown by arc fusion. They also found a strong emission peak at 4500 Å, most likely due to F-center excitation [12]. Past AFIT research into oxidation of UO_2 powder using PL highlighted the presence of higher oxidation states but did not investigate the defects responsible [13].

More recent research into AFRL-grown single crystal UO_2 using x-ray diffraction (XRD) has shown that nearly stoichiometric UO_2 is in the fluorite structure and highly pure. These XRD measurements indicate a nominal lattice parameter for $\text{UO}_{2.003}$ of 5.4703 ± 0.0006 Å [14], which is in excellent agreement with the body of UO_2 lattice parameter research as outlined by Leinders *et al.* [15]. This research also provides temperature-dependent Debye temperatures supporting strong lattice-phonon interactions [14].

2.3 UO₂ Crystal Structure, Bonding, and Electronic Structure

UO₂ crystallizes in a face-centered cubic (fcc) structure similar to that of fluorite. Uranium cations (U⁴⁺) occupy the face-centered sites that surround eight cubic-coordinated oxygen ions (O²⁻). The fluorite structure is depicted in Figure 1 with the black atoms as the uranium cations and the white atoms as the oxygen anions. There are 12 lattice vacancies at ($\frac{1}{2}$, 0, 0) along each cell edge and one located in the cube's center ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) depicted as white squares. The length of each face, lattice parameter, is measured to be 5.471 Å for UO₂ at room temperature [15], with interatomic distances of 3.868 Å for U⁴⁺ - U⁴⁺, 2.735 Å for O²⁻ - O²⁻, and 2.369 Å for U⁴⁺ - O²⁻ [16].

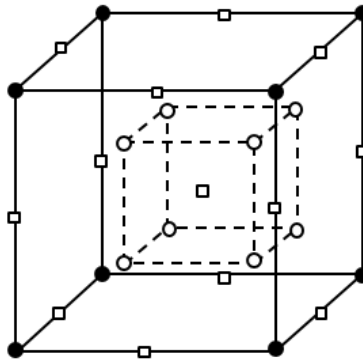


Figure 1. Unit cell of face-centered cubic crystal UO₂. Oxygen anions are represented by white circles, while uranium cations are represented by black circles. Holes in the fluorite structure are represented by white squares. Figure adapted from C.A. Colmernaes [17].

2.4 UO₂ Electronic Structure

The electronic structure of UO₂ will now be explored. A flawed understanding of what the preponderance of peer-reviewed literature establishes as the electronic structure will lead to flawed analysis of the luminescence arising from the transitions contained therein. The following section begins by first breaking down the differences in published

band gap values. Then consideration is given to the crystal effects that establish the conduction and valence bands as reported in the literature. Finally, the UO_2 electronic structure is concluded with a brief discussion on the near-identical electronic structures of some of the analogous lanthanide oxides.

Uranium is an exception to the Aufbau and Madelung rules that predict the electron orbital filling order. Its electron orbital configuration is $[\text{Rn}] 7s^2 5f^3 6d^1$. The chemical behavior of the lighter actinides is a sharp departure from that of their analogous 4f lanthanides due to there being a high number of different electronic configurations resulting from so many 5f electrons having similar wavefunctions. This allows for uranium's unfilled 5f orbital to hybridize with the unfilled 6d, 7s, and oxygen's 2p orbitals, giving solid uranium a range of possible oxidation states from +3 to +6 [18]. In UO_2 , the difference in electronegativity between the uranium and two oxygen atoms results in four electrons ($7s^2 5f^3 6d^1 \rightarrow 5f^2 + 4e^-$) being transferred to oxygen forming the ionic bonds of the molecule. The conduction band is therefore comprised mainly of the 7s6d uranium electrons and the valence band of the 2p oxygen electrons. Both bands strongly hybridize with the 5f electrons.

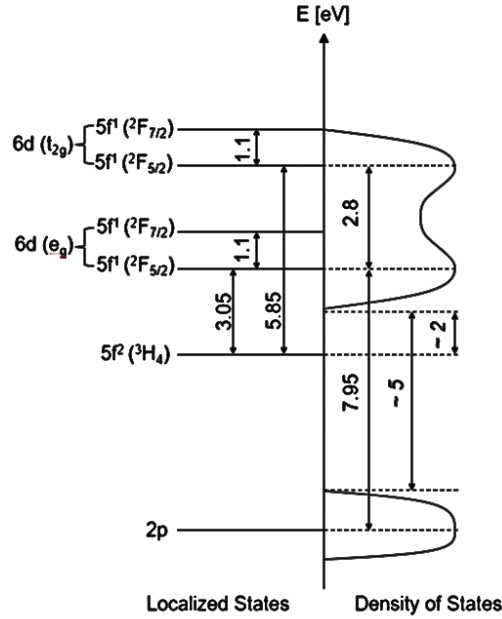


Figure 2. Optically derived UO₂ electronic structure at 300 K. Figure adapted from Schoenes [19]. *Italicized numbers are derived; non-italicized numbers are reported by Schoenes.*

The most widely cited empirical model of UO₂'s electronic structure was put forth by Schoenes [19]. The electronic structure diagram shown in Figure 2 depicts the 7s5f6d-localized states in the left vertical column, while the 7s5f6d conduction band and the 2p valence band are shown on the right. Term symbols representing Russel-Saunders coupling, or LS coupling, is included in parenthesis for each state. Schoenes constructed the diagram using his own analysis on both the real and imaginary UO₂ dielectric constant [19]. He determined that UO₂'s optical properties are governed by two sets of transitions. The lower energy transition, approximately 2 eV, he argues, is that from a narrow 5f² state to the conduction band, while the larger, approximately 5 eV is that of the 2p valence band to the conduction band. This is in agreement with his transmission spectroscopy work where he showed two strong absorption edges at $E_1 \approx 2$ eV and $E_2 \approx 5$

eV [19], and from the theoretical calculations. This separation of the 5f orbital state from the 6d orbital that results from hybridization make UO_2 a Mott-Hubbard insulator [20].

The additional literature that follows in Table 1 has either experimentally examined or theoretically calculated the band gap of UO_2 . The differences and uncertainty in experimentally reported values are most likely the result of differences in technique, sample porosity, uncertainties in measured thicknesses, variations in surface roughness, and slight deviations from stoichiometry. Others have theoretically calculated the band gap using variations of Density Functional Theory (DFT) computational modeling. Such variations include DFT+U (Hubbard correctional term), Generalized Gradient Approximation with Hubbard correctional term (GGA+U), Local Density Approximation with Hubbard correctional term (LDA+U), and Heyd-Scuseria-Ernzerhof screen hybrid density functional theory (HSE) with and without spin-orbit coupling (SOC). This list is not exhaustive.

Table 1. Published Band Gaps for UO₂ and higher oxidation states. Energies in eV.

Author	Method	UO ₂
Meek <i>et al.</i> [21]	Exp.	2.0-2.5
Kelly & Brooks [22]	LDA	5.35
Baer & Schoenes [23]	Exp.	5.0±0.4
J. Wang <i>et al.</i> [24]	DFT+U	1.9
H. Shi <i>et al.</i> [25]	GGA+U	2.3 / 5.53
H. He <i>et al.</i> [26]	LDA+U	2.27
	HSE	2.71
X. D. Wen <i>et al.</i> [27]	HSE	2.4
	HSE+SOC	2.4
B. Dorado <i>et al.</i> [28]	DFT+U	2.3
J. Schoenes [29]	Exp.	~2.0
[19]	Exp.	2.1

It is important to note the difference between these reported values and that from Schoenes's work. Meek *et al.* experimentally determined the band gap through absorption spectroscopy on thin films. Never once does his work discuss whether their results represent the $5f^2 \rightarrow 5f^1 6d^1$ transition or those of the $2p \rightarrow 5f^1 6d^1$ band gap, nor do they cite Schoenes's work. Kelly and Brooks explicitly state the calculated $2p \rightarrow 5f^1 6d^1$ band gap is 5.35 eV, while Baer and Schoenes, through electron photospectroscopy (XPS), experimentally determine the $2p \rightarrow 5f^1 6d$ band gap is 5.0 eV. J. Wang *et al.*'s work makes the clarification that the band gap they calculate is actually that of the $5f^2 \rightarrow 5f^1 6d$ transition, as they compare their results to those of Schoenes's experimental results [19]. H. Shi *et al.* calculated both gaps with good agreement with Schoenes's work [25]. H. He *et al.*, X. D. Wen *et al.*, and B. Dorado *et al.*, each attribute their group's findings to $5f^2 \rightarrow 5f^1 6d^1$ transitions but provide no calculation to the $2p \rightarrow 5f^1 6d^1$ band gap [26] [27] [28].

The reason for the clarification is the term "band gap" is often used without explanation. Without the knowledge that UO₂ is a Mott-Hubbard insulator with the

intermediate $5f^2$ band between the conduction and valence band, a reader would be tempted to think the band gap, as traditionally thought, is approximately 2 eV and would then come to expect to see that manifested in optical experimentation. However, the crystal field splitting of the 6d orbital and hybridization of the O 2p orbital with the U 5f orbital results in the onset of the $5f \rightarrow 6d$ and $5f \rightarrow 5f$ transitions beginning around 2 eV, as shown in the reference literature above.

The d orbitals are five-fold degenerate. As the uranium and oxygens come together, the oxygen's electrons will repel the five-fold degenerate d orbital electrons. The three-fold orbitals (d_{xy} , d_{xz} , d_{yy}) will split from the two-fold (d_z^2 and $d_{x^2-y^2}$) orbitals, represented by t_{2g} and e_g in Figure 2 respectively. In a tetrahedral complex such as UO_2 , the doublet, or e_g orbitals, are repelled more, resulting in a greater distance between them and the ligand electrons than between the triplet, t_{2g} orbitals and the ligand's electrons. Thus, the five-fold degenerate 6d orbitals split with the doublet lower in energy compared to the triplet. Schoenes's study also showed the crystal field splitting of the f-d conduction band between its $5f^1 6d^1(t_{2g})$ and the $5f^1 6d^1(e_g)$ parts by 2.8 eV, and the spin-orbit splitting of both $5f^1(^2F)$ final states into $^2F_{7/2}$ and $^2F_{5/2}$ halves separated by 1.1 eV [19]. Gajek *et al.* both calculated and experimentally showed the various energy levels of U^{4+} putting them in agreement with Schoenes [30].

2.5 Defects

Defects in solids are broken down into four basic categories: point defects, line defects (one-dimensional), planar defects (two-dimensional), or volume defects (three-dimensional). For the purpose of this research, only point defects will be properly

investigated, though with an understanding that line and planar defects on the sample's surface may have significant impacts on CL and PL data. Point defects can be further subdivided into vacancies, interstitials, and substitutions. Vacancies and interstitials are partly responsible for the observed electrical conductivity of materials [31]. Their introduction into a perfect crystal raises the crystal's free energy by the defect's formation energy, E_f .

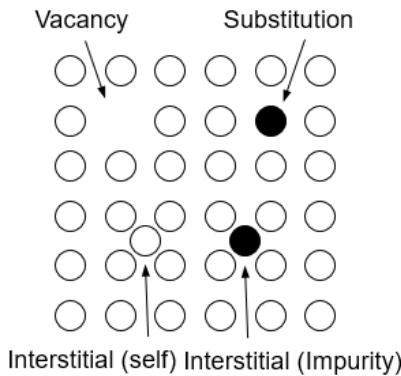


Figure 3. Generic depiction of native and foreign point defects.

Vacancies are formed when an atom is removed from its position in the lattice and placed elsewhere as shown in Figure 3. UO_2 is a diatomic molecule with both oxygen and uranium vacancies. Cationic and anionic vacancies occur in almost stoichiometric numbers in order to maintain localized charge neutrality. Thus for UO_2 , each uranium vacancy corresponds to two oxygen vacancies. This triplet is called a Schottky trio [32]. Petit *et al.* performed UO_2 formation energy calculations using a variation of density-functional theory. They calculated the formation energies for oxygen vacancies, uranium vacancies, and Schottky trios to be 10.0, 19.1, and 14.5 eV respectively [33]. Vacancies are often filled with foreign impurities called a substitution. Anionic vacancies, because of their positive charge, can also capture an electron and form a color center.

Interstitials are atoms inserted into positions in the lattice where they do not belong. These atoms may be either foreign or atoms from the crystal itself. In a solid subjected to particle irradiation, lattice atoms that receive sufficient energy from collisions are ejected from their lattice position. A vacancy and interstitial is created. This pair is known as a Frenkel pair [32]. Additionally, uranium and its decay products are continually decaying, injecting alpha and beta particles into the lattice creating a sequence of nuclear collisions. The resultant recoils lead to a large number of localized lattice defects. For instance, the alpha emitted from the decay of ^{238}U would deposit 4.27 MeV along its path into tens of thousands of neighboring atoms, potentially leaving a cluster of defects in its wake.

Petit *et al.* calculated the formation energies for oxygen interstitials, uranium interstitials, oxygen Frenkel pairs, and uranium Frenkel pairs to be -3.3, 11.5, 5.9, and 22.1 eV respectively [33]. The formation energy for oxygen interstitials is exothermic, and therefore, at a given temperature, the concentration of oxygen interstitials would dominate the defect population. The concentration of oxygen interstitials is also highly sensitive to the temperature. It is therefore reasonable to conclude that exposing UO_2 to air would result in UO_{2+x} . This prediction is in agreement with experimentation [34] [35] [36] and general observation of UO_2 easily oxidizing. At room temperature, surface oxidation dominates and contributes to oxidation of the bulk through oxygen diffusion. However, above 300°C , oxidation is so rapid that oxygen diffusion is nearly uniform [35].

Interstitials generally cause greater disturbances to the lattice structure than do vacancies, and UO_2 is no exception. When the oxygen concentration increases past

stoichiometric UO_2 , additional oxygen atoms fill interstitial sites in the lattice as depicted in Figure 4 [15]. The interstitial oxygen is pulled by the Coulomb force from the uranium atoms, which converts from U^{4+} to U^{5+} to maintain charge balance. The additional electron in the uranium's 6d orbital increases the Coulomb attraction between the nucleus and the inner electrons, thereby contracting the uranium's atomic radius. This contraction, depicted in Figure 4, subsequently causes a contraction on the bond between one or two neighbor lattice oxygens thereby pulling the oxygen atoms from their positions, leaving vacancies [34].

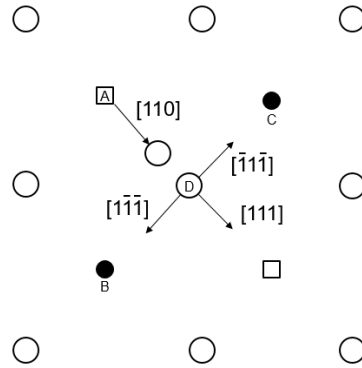


Figure 4. Reaction to interstitial oxygen atoms in UO_{2+x} . The interstitial oxygen enters the structure at A but is pulled along $[110]$ by the Coulomb force from uranium atoms B, C, which convert to U^{4+} to U^{5+} to maintain charge balance. The fluorite-type oxygen at D is displaced, in turn, along one of the $\langle 111 \rangle$ directions shown. Figure adapted from Willis [34].

2.6 Higher Oxidation States

The addition of oxygen interstitials distorts the lattice, creates oxygen vacancies by the process in section 2.5, and increases the stoichiometry to UO_{2+x} . The cluster of two oxygen vacancies, two oxygen interstitials of one kind, and one or two oxygen interstitials of another kind is known as 2:1:2 or 2:2:2 Willis cluster respectively [37].

Experiments have shown that UO_{2+x} stoichiometry can increase up to $\text{UO}_{2.24}$ while still maintaining the fluorite structure [38]. However, beyond $\text{UO}_{2.25}$, the 2:2:2 Willis clusters ordered throughout the lattice increase the lattice volume 64 times that of the stoichiometric UO_2 fluorite cell changing the cell geometry [37]. Further oxygen incorporation beyond $\text{UO}_{2.24}$ results in U_4O_9 . Still more oxygen results in a slight but systematic displacement of the uranium atoms distorting the unit cell from cubic symmetry to tetragonal, producing U_3O_7 , and ultimately to orthorhombic symmetry [39]. At this point, the O/U has increased between 2.37 to 2.5, producing U_2O_5 , U_4O_9 , U_3O_7 , and U_2O_5 and has a number of different phases associated with each that corresponds to a more specific U/O ratio.

At a U/O ratio of 2.66, $\alpha\text{-U}_3\text{O}_8$ is formed. The uranium oxidation state in UO_2 is U^{4+} . However, in U_3O_8 , the oxidation states of the uranium may be either $2x \text{U}^{6+} + 1x \text{U}^{4+}$ or $2x \text{U}^{5+} + 1x \text{U}^{6+}$ [18]. The incorporation of these higher oxidation state uranium atoms create uranyl ions (UO_2^{2+}) with U-O bonds shorter than that of UO_2 . These compounds cause the packing arrangement of the uranium atoms in the unit cell to shift the fluorite to a layered structure such that each uranium atom is directly above the oxygen atom in the layer below. This increases the atomic spacing, which results in an increase in lattice volume and, thereby, a decrease in crystal density. It is this drastic shift in the structure that is the cause of the deformation of UO_2 fuel pellets [39]. $\alpha\text{-U}_3\text{O}_8$ is the stable phase of U_3O_8 at room temperature [17].

2.7 Luminescence

2.7.1 Overview

Luminescence is the emission of a photon from a solid, in this case a semiconductor, when valence band electrons, have been excited into the conduction band and undergo one of many radiative or non-radiative transitions and de-excite back into the valence band to recombine with a hole. Non-radiative transitions may be of the form of multiple-phonon emission, emission of Auger electrons, or recombination due to surface defects. In radiative transitions, if the electrons transition directly back to the valence band within $\sim 10^{-8}$ seconds, the emitted photon is referred to as fluorescence, whereas a delay in the transition will result in phosphorescence [40]. The energy, or wavelength of that photon, will depend upon the material (in this case UO_2), its purity, and the presence of defects in the lattice. Broad luminescence emission peaks are often the result of strong electronic and phonon coupling or from point defects serving as electron/hole traps.

2.7.2 Non-Radiative Transitions

Phonons

The balance between the Pauli repulsion and the bonding attraction creates a stable bond length. The potential energy of the nuclei and, subsequently, the whole crystal system, can be modeled as a spring. If thought as a diatomic linear chain, in-phase motion of the two masses is referred to as acoustical vibration. If the two masses have different charges, then motion out-of-phase produces an oscillating dipole that can absorb

and emit electromagnetic radiation. This is known as optical vibration. If the atomic motion is parallel to the propagation direction, then the vibrational wave through the system is longitudinal, while perpendicular oscillation is transverse. In three dimensions, there are two transverse vibrational waves for every longitudinal [41]. It is these vibrational motions that are the main contributors to the heat capacity and the mechanism of heat conduction of the crystal [41].

As with light, these vibrations have a quasi-particle nature and can be represented quantum mechanically as a superposition of harmonic oscillator vibrations. The energy and momentum are, respectively, equal to $\hbar\omega$ and $\hbar q$, where q is the wave vector and ω is the wave frequency [41]. Any phonon-coupled transitions can be calculated as follows.

$$E = E_g - n\hbar\omega \quad (1)$$

$$\begin{aligned} E_g &= \text{Energy of band gap} \\ \hbar &= \text{Planck's constant } (6.58 \times 10^{-16} \text{ eV}\cdot\text{s}) \\ n &= \text{Quantum number} \end{aligned}$$

Based on (1), transitions that are not phonon-coupled (i.e., $n = 0$) are called the zero-phonon line (ZPL). Quantum numbers one and higher produce what is known as phonon replicas. These are distinguishable from the ZPL as a series of emission lines exactly $\hbar\omega$ apart. With the introduction of defects into a theoretically perfect crystal, translation symmetry is broken, energy levels appear in the band gap, and, as a result, new vibrational modes appear.

Table 2 presents some experimentally determined, as well as theoretically calculated, phonon frequencies for UO_2 . Values are presented in wavenumbers [cm^{-1}], phonon frequency (THz), or energy (meV). Wavenumbers are converted to frequencies as follows.

$$\frac{1}{\lambda} = \frac{\omega}{(2\pi)c} \quad (2)$$

c = Speed of light in vacuum [$\sim 3 \times 10^{10}$ cm/s]

Table 2. Published phonon frequencies and energies (Bolded), derived numbers from (2) (Italicized).

Author	ω_{TO} [cm ⁻¹]	ω_{TO} [THz]	E_{TO} [meV]	ω_{LO} [cm ⁻¹]	ω_{LO} [THz]	E_{LO} [meV]
Schoenes [29]	280	<i>8.40</i>	<i>34.73</i>	578	<i>17.34</i>	<i>71.69</i>
Axe & Petitt [42]	278	<i>8.34</i>	<i>34.48</i>	556	<i>16.68</i>	<i>68.96</i>
Dolling <i>et al.</i> [43]	284	<i>8.52</i>	<i>35.22</i>	557	<i>16.71</i>	<i>69.09</i>
Pang <i>et al.</i> [44]	<i>273.52</i>	<i>8.21</i>	33.93	<i>436.99</i>	<i>13.11</i>	54.20
Yun <i>et al.</i> [45]	<i>283</i>	8.49	<i>35.11</i>	<i>527.33</i>	15.82	<i>65.42</i>

Surface Recombination

Uranium and oxygen atoms at the surface of the crystal do not have the same bonding structure as those in the bulk due to the abrupt end of neighboring atoms. As there are no more atoms to bond to, the valence orbitals of these atoms on the edge of the structure go partially or completely unfilled. These dangling bonds are electronic states that can be located in the band gap energetically where they serve as deep level recombination centers. Thus, surface recombination reduces luminescence efficiency.

Auger Electrons

Band-to-band Auger recombination is when an electron and hole recombine, but the subsequent released energy does not optically radiate. Rather, the emission energy excites another electron higher in the conduction band to where it then energetically decays via phonon emission back toward the conduction band minimum. The Auger effect can explain why optical radiative emission does not occur when it should. Its prevalence increases with increased carrier concentration.

2.7.3 Radiative Transitions

Intrinsic

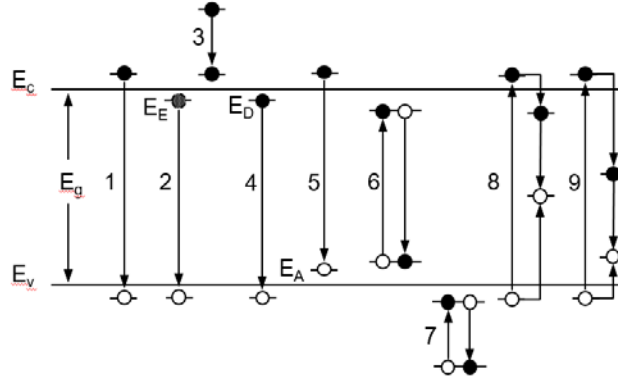


Figure 5. Generic depiction of radiative transitions between conduction band (E_c), valence band (E_v), exciton (E_e), donor (E_d), and acceptor (E_a) levels across the band gap (E_g) [40].

It is helpful to divide radiative emission into two categories: (1) intrinsic or edge emission and (2) extrinsic, activated, or characteristic emission. Intrinsic emission is due to the recombination of electrons and holes between the conduction band minimum state and valence band maximum state producing a photon of energy equal to the width of the band gap, $E_g = h\nu$, depicted as transition 1 in Figure 5. When the hole is at a valence band maximum, the electron at a conduction band minimum, and both possess identical quantum wave vectors, the transitions are direct band-to-band transitions. When the wave vectors differ, the transitions are indirect band-to-band transitions, as in silicon. To conserve energy and momentum in indirect transitions, photons are accompanied by the emission of phonons. However, this process is three to four orders of magnitude less probable than direct transitions; therefore, intrinsic emission in indirect-gap semiconductors is weak compared to that of direct-gap semiconductors [46]. A carrier

may also undergo intraband transition where, as depicted as transition 3 in Figure 5, an electron excited well above the conduction band trickles down toward thermal equilibrium.

Another form of intrinsic luminescence that usually occurs at low temperatures is the emission from recombination of a bound electron-hole pair: an exciton. It is due to the electron-hole Coulombic interaction that brings their energy levels closer together, producing an energy state just below the conduction band, and optically produces a series of sharp emission lines. The spacing between the lines can be calculated using (3) and for excitons, (4) [46] [47].

$$E_n = E_g - E_B/n^2 \quad (3)$$

$$\begin{aligned} E_g &= \text{Band gap} \\ E_B &= \text{Exciton binding energy} \\ n &= \text{Quantum mechanical state} \end{aligned}$$

$$E_B = \frac{\mu e^4}{8\epsilon^2 h^2 n^2} \quad (4)$$

$$\begin{aligned} \mu &= \text{Exciton reduced mass} \\ \epsilon &= \text{Static dielectric constant} \\ h &= \text{Planck's constant } (4.135 \times 10^{-15} \text{ eV}\cdot\text{s}) \end{aligned}$$

These transition lines can be complicated when coupled with phonons. Emission generally results from excitons bound to neutral donors/acceptors. Bound exciton's emission lines are lower in energy than free excitons by an amount corresponding to the exciton-impurity binding energy [46]. Free excitons are rare. Since momentum must be conserved during the transition, this is usually accomplished thanks to accompanying phonon emission. Shown as transition 2 in Figure 5, the exciton recombination produces a photon similar to that of direct band-to-band recombination, albeit at a lower energy

than E_g . Self-trapped excitons (STE) are those that are neither free nor bound to a donor/acceptor but rather are trapped by their own self-induced lattice distortion [47]. STEs are typically characterized by strong phonon coupling, and as a result, are found well below the band gap. STEs produce a broad Gaussian emission peak at room temperature but tend to produce more of a Lorentzian peak at lower temperatures [47].

Excitons may be categorized as either Wannier or Frenkel. Wannier excitons are those whose wave functions are larger than that of the lattice constant [46]. Wannier excitons are typically only found at low temperatures when their binding energy exceeds thermal energy. A Frenkel exciton's wave functions are smaller than the lattice constant and are typically organic complexes.

Extrinsic

Any emission spectra that arise from the presence of impurities is referred to as extrinsic emission and is characteristic of that particular impurity. Transitions 4 and 5 in Figure 5 depict unlocalized transitions that start and/or stop at impurity sites in the band gap. As the name suggests, localized extrinsic emission is confined to isolated areas in the lattice due to localized impurities, often intentionally incorporated. Localized transitions can be subdivided into allowed-type (i.e., orbital transitions $s \leftrightarrow p$, $s^2 \leftrightarrow sp$, $f \leftrightarrow d$) shown as transition 7 in Figure 5 and forbidden-type (i.e., orbital transitions $d \leftrightarrow d$, $f \leftrightarrow f$) shown as transition 6 in Figure 5.

Transitions within the 5f orbital (i.e., $5f \leftrightarrow 5f$) are strictly forbidden because parity does not change. Based on the angular quantum number (Δl) selection rule, electric dipole transitions between similar parities are forbidden. However, perturbations in the

local crystal electric field (e.g., induced dipoles in the ligands) can partially allow forbidden transitions. Where the crystal structure does not have inverse symmetry, the local crystal electric field adds the necessary odd component to angular momentum. By this addition from the perturbation, the dipole transition forbidden by the transition parity rule is now allowed. Transitions between orbitals such as $f \leftrightarrow d$, as in $5f^2 \leftrightarrow 5f^1 6d^1$, are allowed as both transition rules are obeyed. A strong crystal field greatly affects such transitions by inducing splitting of the 5d orbitals into different energy levels. Spectroscopically, this results in a large, broad band. The $f \leftrightarrow f$ transitions are not as coupled to the crystal field and, as a result, are typically more well-resolved (equipment dependent) but less intense due to their forbidden nature and at lower energies than those of the allowed variety.

Transitions 8 and 9, known as donor-acceptor pair (DAP) transitions, depict the start and stop of a transition within the gap or within the band respectively. These transitions can be seen as an intermediate type between localized and unlocalized types. Here, an electron captured by a donor under the conduction band recombines with a hole captured by an acceptor above the valence band. DAP emission energies can be calculated using (5) [47].

$$E_{DAP} = E_g - (E_A + E_D) + \frac{e^2}{\epsilon r} \quad (5)$$

$E_{A/D}$ = Acceptor/Donor energy
 ϵ = Refractive index (small r) / static dielectric constant (large r)
 r = Distance between donor and acceptor

Since r is limited to certain values dependent upon material properties, DAP emission produces sharp emission lines whose sharpness increases with decreasing r . Discrimination of DAP emission lines from other forms of emission can occur by

increasing the beam power of the investigation source (i.e., CL or PL). Increasing beam power shifts DAP emission lines to higher energy as large r DAP centers saturate and small r DAP centers dominate [47].

2.7.4 $5f^16d^1 \rightarrow 5f^2$ and $5f \rightarrow 5f$ Transition Luminescence

Much work has been done on the emission spectra arising from $4f \leftrightarrow 5d$ transitions of the lanthanides Ce^{3+} , Pr^{3+} , and Eu^{3+} for their possible application as tunable lasers, activators in scintillation crystals, and various other technologies. These elements are analogous to the lighter actinides, especially uranium. Strong luminescence bands of these elements are credited to the strongly allowed $4f \leftrightarrow 5d$ with less intense, albeit more highly resolved, bands at lower energies credited to Laporte forbidden $4f \rightarrow 4f$ transitions. Like many lanthanides, uranium produces luminescence owing to the $5f \rightarrow 5f$ transition in the visible or IR region and $5f \rightarrow 6d$ transitions in the visible and UV regions. $5f$ electrons are located inside the $7s6d$ shells, so the influence of the crystal electric field on the $5f$ shell is much weaker than on the $6d$ shell. Therefore, $5f \rightarrow 5f$ transitions will tend to have more narrow emission peaks. For example, Simoni *et al.* and Genet *et al.* measured the $5f \rightarrow 5f$ Laporte forbidden transitions of $ThBr_4:U$ providing exceptionally well-resolved peaks [48] [49].

For help illustrating the interconnectedness of $5f^16d^1 \rightarrow 5f^2$ and $5f \rightarrow 5f$ transitions, the optically derived UO_2 electronic structure presented in Figure 2 is modified to provide more detail in Figure 6. It is important to note that Figure 6 is not to scale, not all possible $5f^2$ microstates are shown, and of those $5f^2$ microstates shown, only those $5f^16d^1 \rightarrow 5f^2$ transitions allowed by quantum transition rules are shown.

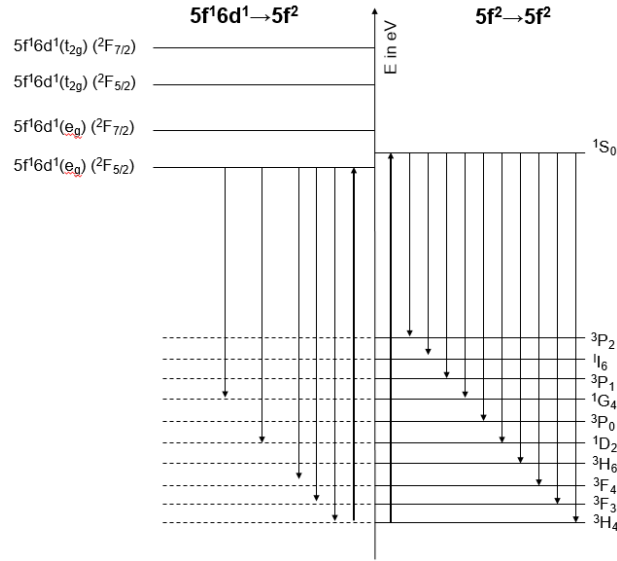


Figure 6. Electronic structure of likely $5f^1 6d^1 \rightarrow 5f^2$ and $5f \rightarrow 5f$ transitions

Kirm *et al.* noted that when the lowest level $5f^1 6d^1$ state lies below the highest $5f^2$ excited state ($^1S_0$), as in the case of $\text{LiYF}_4:\text{U}^{4+}$, the dominate channel for radiative transition is $5f^1 6d^1 \rightarrow 5f^2$. When the lowest level $5f^1 6d^1$ state lies above the highest $5f^2$ excited state ($^1S_0$), as in $\text{LiF}_3:\text{U}^{4+}$, $5f \rightarrow 5f$ luminescence is the dominate radiative transition [50]. In this case, electrons in the lowest level $5f^1 6d^1$ state vibrationally deexcite to the $^1S_0$ state before the $5f \rightarrow 5f$ transition. Kirishima *et al.* conclude in their study that the lowest level $5f^1 6d^1$ state of U^{4+} in perchlorate solution lies above the highest $5f^2$ excited state ($^1S_0$) and that these values represent $5f \rightarrow 5f$ transition [51]. This is supported by the fact that their peaks are highly resolved. They observed 12 broad emission peaks. Four intense peaks at 319, 335, 410, and 525 nm, and eight weak peaks at 289, 292, 313, 321, 339, 346, 394, and 447 nm [51].

Other studies have looked at compounds doped with U^{4+} . Godbole *et al.* conducted both absorption and emission luminescence studies on single crystal $\text{LiYF}_4:\text{U}$

using spectrophotometers equipped with flash lamps. Their absorption spectra showed peaks from 211.8 to 255.2 nm. This is in excellent agreement with Hubert *et al.* and are attributed to the 5f-6d transitions [52]. The resultant emission spectra using 242 nm excitation showed five strong, broad peaks from 262 to 334 nm attributed to the 5f-6d transitions and two weak peaks at 430 and 490 nm attributed to 5f→5f Laporte forbidden transitions from the 5f² ground state (³H₄) to 5f² excited states [53]. A similar study by Kirikiva *et al.* confirmed Godbole *et al.*'s findings [54].

Behrendt *et al.* conducted an absorption and emission study on single crystal Cs₂NaYCl₆:U using a 1000 W xenon excitation lamp and a 325 nm He-Cd emission laser. The two spectra show a Stokes shift comparable to the ones observed by Godbole *et al.* and Kirikiva *et al.* However, both the absorption and emission peaks are all red-shifted from those studies on LiYF₄:U. There are three large emission peaks at 367, 377, 423 nm and two smaller peaks at 520 and 561 nm. These are attributed to the transitions from 5f¹6d(t_{2g})¹ to either the 5f² ground state (³H₄) or the lower 5f² excited states [55]. Additional experimental and theoretical studies have showed absorption bands in the UV and emission bands in the UV-VIS. However, actual peak wavelengths/energies varied depending upon the ligand or host crystal [56] [57] [58] [59]. These differences most likely result from varying crystal field strengths that produce variations in 5f¹6d splitting. Different host crystals have different field strengths, and thus, the energy levels of the split 5f¹6d states vary, leading to difference in 5f¹6d¹ → 5f² transitions amongst the different materials.

2.7.5 Molecular Vibrational Luminescence

As was discussed in Section 2.6, UO_2 readily oxidizes in the presence of oxygen. As oxygen concentration increases, uranium atoms oxidize from U^{4+} to eventually U^{6+} . This forms the divalent uranyl ion, UO_2^{2+} , in solution or compound in solids. The uranyl compound is a uranyl ion that is a symmetric, linear ion surrounded by an anion forming the secondary U-ligand bond, such as UO_2F_2 as shown in Figure 7.

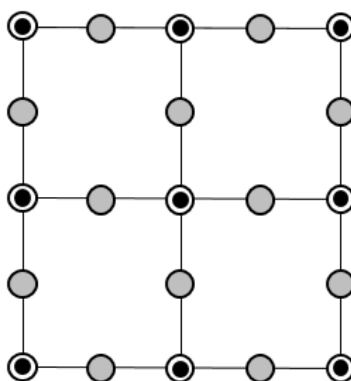


Figure 7. Structure of UO_2F_2 layer. Black circles represent Uranium atoms. White circles represent oxygen atoms bonded to the uranium into and out of the page. Grey circles represent fluorine atoms bonded to the UO_2^{++} ion. Figure adapted from Zachariasen [60].

Here, the uranyl ions are bonded in a sheet across the page, with the secondary U-O bonds extending into and out of the page. This represents the resultant layer structure discussed in Section 2.6. When excited, the three atoms that make up the basic molecule can vibrate as shown in Figure 8.

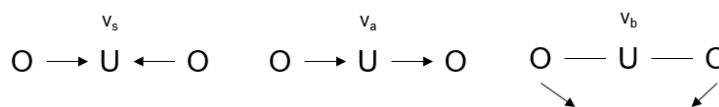


Figure 8. Three uranyl vibration modes. Figure adapted from Rabinowitch [61].

The bending vibration, ν_b , can occur in two mutually exclusive perpendicular planes making it degenerate. It can produce luminescence that is present in IR, visible, and UV emission spectra. The symmetric bond vibrations have no dipole associated with their movement and their luminescence is present in the visible and UV spectra. The antisymmetric vibration is absent in the Raman spectrum. These exclusion rules are only valid for a free ion in solution. The vibrations can be assumed to be harmonic such that (6) – (8) can be used [61].

$$\nu_s = \sqrt{f/m_o} \quad (6)$$

$$\nu_a = \sqrt{f/m_o (1 + 2m_o/m_u)} \quad (7)$$

$$\nu_b = \sqrt{2d/f (1 + 2m_o/m_u)} \quad (8)$$

In (6) - (8), f = elastic force constant in line with the bond, d = distance in direction perpendicular to the bond, m_o = mass of oxygen, and m_u = mass of uranium.

Since m_o is approximately 15x smaller than m_u , it follows that ν_a is approximately 6% larger than ν_s , which corresponds to the stable ν_s and ν_a literature ranges of approximately 700 to 900 cm^{-1} and 800 to 1000 cm^{-1} respectively [62]. Because $d \ll f$, ν_b is considerably smaller than the other two at approximately 220 cm^{-1} [61]. The symmetric vibrations contribute most to emission spectra as follows. The electrons that form the bonds are excited and the bonds stretch beyond the equilibrium bond length, and as the excited electrons relax and luminesce, the bonds contract like a spring and vibrate. With each vibration, the bonds stretch back out, and then fluoresce again as the bonds contract back toward equilibrium. Since the oxygen atoms move in tandem for antisymmetric vibrations, one toward the uranium atom and one away, no overall

potential energy is lost, therefore antisymmetric vibrations do not occur from electronic excitation unless the bond deviates from elasticity. The bending vibrations are also little affected by electronic excitation unless the bonds deviate from linearity.

The overall emitted luminescence spectrum of the uranyl ion can be calculated using (9) [61].

$$v_{fluorescence} = v_f - n_s v_s - n_a v_a - n_b v_b - \sum n_i v_i \quad (9)$$

In (9), v_f = pure electronic transition, n_s = quanta of symmetric vibration excited simultaneously with v_f (0 to 8), v_s = symmetric vibration, $n_{a/b}$ = 0 or 1 (only allowed antisymmetric/bending quanta for luminescence), v_a = antisymmetric vibration, v_b = bending vibration, and $\sum n_i v_i$ = vibration related to associated anions or to crystal itself.

Much work has been done on the emission of uranyl dating back to the mid-1800s. Dieke and Duncan's work published in the National Nuclear Energy Series following the Manhattan Project, which catalogs the emission spectra of a large number of uranyl compounds, serves as the literary guide to assessing whether vibrational frequencies fall within the acceptable range [63].

III. Methodology

3.1 Overview

This chapter is subdivided into seven overall sections. The first two sections provide an overview of the samples and data acquisition process. The next two sections detail the theory, specific equipment used, and the experimental techniques used to gain insight into what specific extrinsic impurities may be present in the samples. The following two sections detail the theory, specific equipment used, and the experimental techniques used to investigate what defects were present in the samples. The last section discusses the theory, system, and experiment techniques used to irradiate the sample with neutrons to induce fission. Where applicable, any modeling used to assist in the experimental technique will be presented in full.

3.2 Samples

The single crystal UO_2 samples currently being researched by both AFIT and AFRL are grown via a hydrothermal growth method that produces highly ordered crystalline structures. Initial crystals were grown on calcium fluoride (CaF_2) seed crystals due to the small mismatch in their lattice parameters, ensuring sufficient UO_2 adhesion. However, the CaF_2 bond strength is significantly weaker than that found in UO_2 , which results in lattice strain between the two compounds, causing the resultant crystal to be excessively brittle. CaF_2 was replaced with ThO_2 , which has a similar lattice parameter and bond strength to UO_2 . The resulting crystal growth produced a uranium-thorium

oxide mixed layer on the seed crystal surface. The ThO_2 seed crystal was then cut away, allowing the UO_2 crystal to serve as the next seed crystal for additional growth or for immediate experimentation and analysis.



Figure 9. Dimensions of samples UO_2 -T-93B, -93D, and -93E.

This experiment examined three crystal samples. UO_2 -T-93B, -93D, and -93E. Each sample, pictured in Figure 9, is (100) crystallographically oriented. Chosen for its smoothness and lack of visual defects relative to the opposite face, the face pictured is the surface used for measurements and, hereafter, is referred to as the alpha side. The opposite is referred to as the beta side. Due to an excessive amount of thorium on the beta side of 93B, that side was additionally polished to remove the thorium. This was done to ensure the sample did not break at cryogenic temperatures.

3.3 Approach

The overall scheme of operation for this experiment is presented. Each task is itemized in the nominal order of occurrence, along with its purpose and expected

outcome. Steps 1 and 2, and steps 3 and 4 can be interchanged based on availability of equipment, but the process is defined by experimental efficiency based on location of the samples and equipment, and the desire to take CL and PL measurements with an established expectation of existing impurities. Following irradiation, this process is repeated in the same order.

1. XRF

- a. Task: XRF scan nine evenly spaced locations spanning the approximate area of a standard CL electron beam or PL photon beam on both sample faces at 30 keV for 600 seconds each.
- b. Purpose: Gain an understanding of what extrinsic impurities exist in the material.

2. HPGe Gamma Spectroscopy

- a. Task: Gather a 24-hour gamma spectrum of each sample centered directly onto detector housing.
- b. Purpose: Gain additional understanding of what extrinsic impurities exist in the material. Compare results with those from XRF.

3. Cathodoluminescence

- a. Task: Perform CL on each sample's alpha face at 36 K from 2000 to 8000 Å.
- b. Purpose: Identify surface point defects that exists, and compare results to that of literature.

4. Photoluminescence

- a. Task: Perform PL on each sample's alpha face at 10 K from 3450 to 6450 Å.
- b. Purpose: Identify surface point defects that exist. Compare results to that of CL and literature.

5. Irradiation

- a. Task: Induce fission from neutron irradiation.
- b. Purpose: Create greater than 10^{14} defects per cm^3 in the sample so that changes in defects can be detected and analyzed with CL and PL measurements.

3.4 XRF

3.4.1 Theory

X-ray fluorescence, XRF, is a technique that can determine elemental composition of a sample surface. X-rays emitted from a rhodium filament are incident on the sample and excite electrons in either the K ($n=1$), L ($n=2$), or M ($n=3$) orbitals. These electrons are ejected from their orbitals. Electrons from higher orbitals drop down to fill the hole, emitting a material-specific characteristic x-ray as shown in Figure 10. A competing process to fill this vacancy is the Auger effect. Therefore, the intensity of the emitted x-rays are dependent upon the fluorescence yield of that material. The fluorescence yield for higher Z elements is close to one and approaches zero for lower Z elements [64].

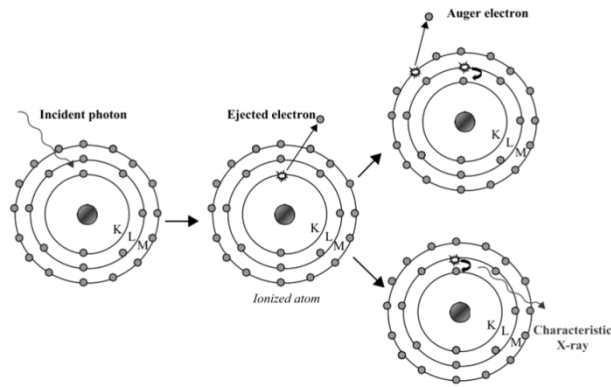


Figure 10. Process of atom ionization and x-ray characteristic emission [64].

The characteristic x-ray emission is related to the atomic number, Z , of the material through the law of Henry Moseley as in (10).

$$\frac{1}{\lambda} = K \times (Z - \sigma)^2 \quad (10)$$

K and σ are element specific constants that specify the energy distribution levels and sublevels involved in orbital transitions [64]. The wavelength, λ , is related to the energy emitted by (11).

$$\lambda = \frac{hc}{E} \quad (11)$$

In (11), h is Planck's constant and c is the light speed constant. As touched upon in Section 2.7.3, some electron transitions between orbitals are forbidden while others are allowed based on the law of quantum mechanics. Allowed characteristic x-ray transitions for uranium are shown in Figure 11.

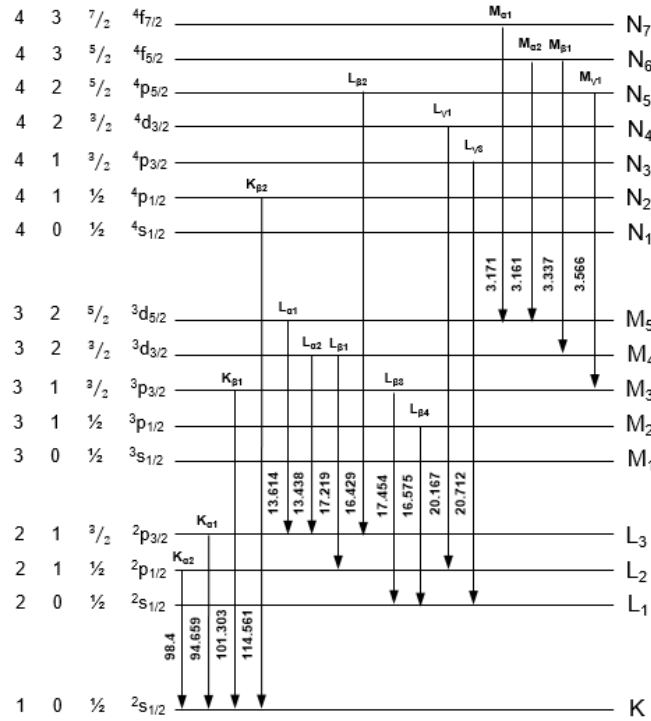


Figure 11. Principal allowed transitions producing x-ray characteristic emission for uranium.

To achieve x-ray emission, the excitation energy must be larger than the absorption edge for the corresponding group of lines of each element. The spectra of x-

rays are collected and used to determine the species of elements present in the sample. The XRF system has a detection range from sodium to uranium. However, the XRF system only allows for x-ray energies of 15, 30, and 50 keV. If 15 keV is chosen, there will be lower background noise and improved signal-to-noise ratio for peaks in the low energy range (i.e., lower Z elements). The x-rays are emitted from a rhodium filament. Because rhodium is extremely rare in nature, any detection of rhodium will likely be from those x-rays emitted from the filament.

3.4.2 XRF System

The XRF system consists of a turnkey *Horiba Scientific* XGT-7200 XRF imaging microscope, power supply, and 3-axis controller as shown in Figure 12. X-rays are produced by a rhodium filament and pass through either a 10 or 100 μm capillary inside a lead-lined vacuum chamber. A 5.0×10^{-4} Torr vacuum is maintained by an *ULVAC Kiko Inc.* GLD-201B pump. Samples are positioned on a 3-axis automated shelf. The X-ray voltage setting ranges from 15, 30, or 45 keV. Current ranges from 0.0002 to 1.0 mA. Acquisition time can range from five to 10,000 seconds. The XRF system is capable of a single point to a 1,000-point spectrum acquisition. Spectra are taken and analyzed on *Horiba Scientific* XGT-7000 software.



Figure 12. Horiba Scientific XGT-7200 XRF imaging microscope.

3.4.3 Experimental Techniques

The XRF is calibrated in accordance with the operating manual. A sample of copper is scanned for 500 seconds with 30 keV, 1 mA x-rays. Two characteristic peaks should appear at 8.0 keV and 8.9 keV. Each sample is then centered on the sample shelf with the alpha side facing up. Vacuum is then established. The movable shelf is centered such that the center of the sample is under the x-ray capillary and then elevated until the surface of the sample comes into focus on the microscope camera. Under the microscope, a square grid of nine points is chosen to be investigated from a large area of the surface approximately equal to what the CL beam will cover. Voltage is set to 30 keV and aperture is set to 100 μ m. An acquisition time of 600 seconds for each of the nine points is chosen to provide sufficient peak resolution. Built-in software libraries are used to analyze the resulting spectra to identify impurities. Manual lookup of the elements represented by peak energy is also conducted for comparison. All spectra are uploaded to MATLAB for the spectral reporting presented in this report.

3.5 Gamma Spectroscopy

3.5.1 Gamma Spectroscopy Theory

When a nucleus decays by either beta or alpha decay, the resulting nucleus is not necessarily in its energetic ground state. Often, these nuclei are excited and through gamma-ray emission(s) relax to their ground state as depicted in Figure 13. When these gammas are emitted and detected with a spectroscopy system, information about the radioactive species present can be inferred from the resulting spectrum. The gammas emitted from the decay of most major radioactive isotopes and their daughters are well cataloged. Many produce characteristic gammas at energies that are easily discernable when captured with a high-resolution detector like HPGe. From these spectra, the number of counts and time can be used to calculate the activity. If knowledge of the emission probability of that gamma from that isotope and detector efficiency is available, the concentration of that particular species can be determined.

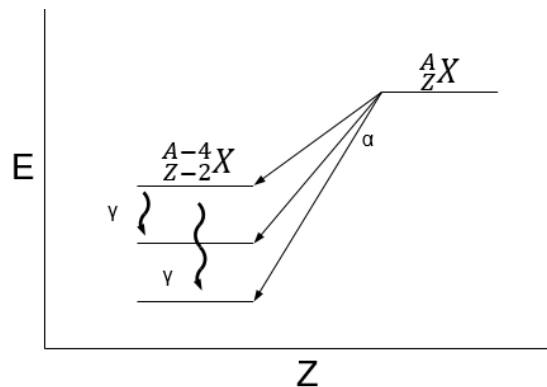


Figure 13. Energy diagram of alpha decay with gamma-ray emission.

3.5.2 Gamma Spectroscopy Modeling

UO₂-T-93B's theoretical gamma spectrum is modeled using the *Gamma Spectrum Generator Pro++* modeling software available at www.nucleonic.com. The sample is assumed to be purely ²³⁸U. The mass in grams of ²³⁸U from the sample is modeled directly on the aluminum crystal housing of thickness 1.5 mm (i.e., no filter separating sample and detector), which sits over a 84.5 mm long by 83.0 mm diameter closed-end coaxial HPGe crystal and is surrounded by 5.0 mm of foam packaging. The detector contact is 9.0 mm wide and is inserted into the crystal by 69.5 mm. These dimensions are those of the actual HPGe detection system used for this research. Figure 14 shows the simulation parameters used while Figure 15 depicts the theoretical 24-hour spectrum. Many of the decay daughters that have prominent gamma emissions have half-lives measured in hours. Twenty-four hours would allow them to undergo at least one half-life. The expectation of what should be present is then compared to HPGe spectrum to help identify impurities.

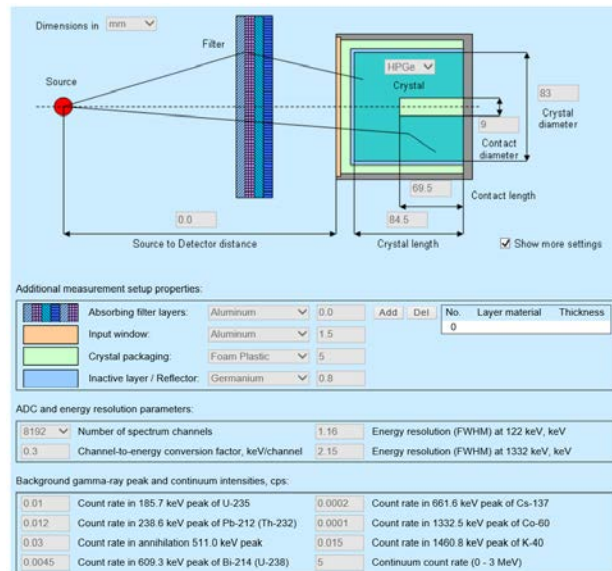


Figure 14. *Gamma Spectrum Generator Pro++* simulation parameters [65].

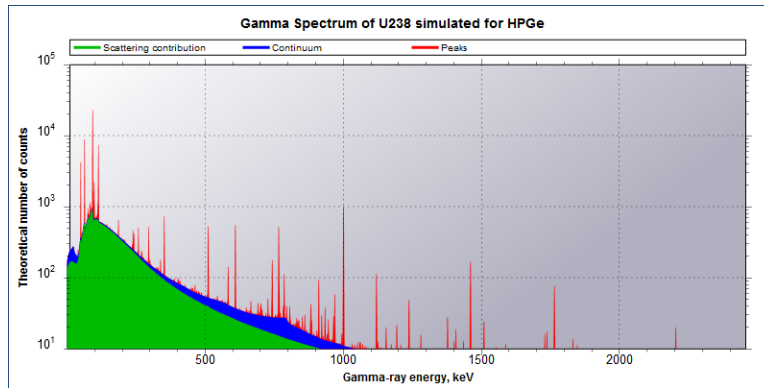


Figure 15. *Gamma Spectrum Generator Pro++* theoretical spectrum [65][66].

3.5.3 Gamma Spectroscopy System

A *Canberra* closed-end coaxial HPGe semiconductor (GC10021) was used for this technique as shown in Figure 16. It is cryogenically cooled to 77 K by liquid nitrogen. For shielding, an outer jacket of 9.5 mm thick low carbon steel surrounds 10 cm of lead. The interior of the shielding is lined with 1 mm tin and 1.6 mm copper. Power is supplied by a *Canberra* DSA 1000 high voltage power supply (HVPS). *Ortec GammaVision™* is the primary method of data acquisition, though another software tool, *Gamma Acquisition and Analysis*, is also used as a means of comparing results.



Figure 16. HPGe Detector assembly mounted over liquid nitrogen dewer.

3.5.4 Gamma Spectroscopy Experiment Techniques

The detector is calibrated using a multinuclide source (T-175) for 24 hours. Then a universal background radiation spectrum is collected for 24 hours prior to any sample. The spectrum of each pre-irradiation sample is then collected for 24 hours. The calibrated background spectrum is then subtracted out from each sample's spectrum leaving only the true sample gamma emission spectrum. Other possible radioactive isotopes that could be present are those from the decay of ^{232}Th and ^{235}U . ^{235}U naturally exists alongside ^{238}U but in small quantities. Serving as the seed crystal, ^{232}Th and its decay chain may be present.

Following irradiation, another 24-hour spectrum is collected. This spectrum is then subtracted from the pre-irradiation spectrum, theoretically revealing the fission fragments and their daughters. The area under full energy peaks, the detector efficiency curve, fission product yields of ^{238}U from fast fission, and decay gamma emission probability as reported in the ENDF/B-VI are then used to calculate the quantity for each

product and daughter. The total calculated number of fissions is then compared to an MCNP6 model, as discussed in Section 3.8.2, as a means of validation.

3.6 Cathodoluminescence

3.6.1 Theory

CL is the luminescence that results from energetic electron excitation. In this experiment, electrons interact in a target material provided by an electron gun. The electrons incident on the sample are far too energetic to excite valence band electrons in the UO_2 . They scatter, leading to the release of x-rays and many secondary electrons (ionization), which in turn leads to the excitation of many more electrons. While many of the incident electrons fully penetrate the material, many more backscatter out of the material. These backscattered electrons are useful in providing surface uniformity information but not for bulk composition. This cascade of scatter events produces up to 10^3 secondary electrons per initial incident electron [67]. CL is advantageous in that it is a non-destructive means of testing. Furthermore, CL is advantageous to other forms of luminescence-based investigation in that it provides high spatial resolution by producing orders-of-magnitude higher carrier generation rates and the ability to obtain more detailed depth-resolved information by varying the electron beam energy [68].

If the absorption edge of the $5f^2 \rightarrow 5f^1 6d$ electron transition starts at ~ 2.0 eV (~ 620 nm) [29], then it makes sense that most of the visible spectrum (~ 620 nm – 400 nm) is absorbed producing a black crystal. If luminescence-generated photons in the visible spectrum are created deep enough in the crystal, they will be absorbed before they

reach the surface. ThO_2 on the other hand is an insulator with a wide band gap and is transparent. Visible wavelengths are not energetic enough to excite valence band electrons into the conduction band and thorium does not show the unique 5f properties that uranium does. As a result, visible light passes through ThO_2 . Because of this fundamental difference, unlike past studies on single crystal ThO_2 using Depth-Resolved CL (DRCL), DRCL on single crystal UO_2 is impractical. The issue is not that energetic electrons cannot penetrate into the crystal lattice; it is that the emitted photons in the bulk cannot escape to be detected. Therefore, defect investigation by CL is limited to the surface conditions of the samples.

Temperature-dependent CL (TDCL) is another application of CL that is also helpful in defect investigation as CL is highly temperature dependent. First, semiconductor band structure and energy states are a function of lattice spacing which contracts and expands with temperature. Secondly, temperature increases result in increased electron-phonon interaction which serves to shift both absorption and emission energies [68]. This allows different electron-hole pair transitions to occur than otherwise would have occurred at low temperature. Unlike DRCL, beam current and voltage are held constant as temperature is varied from low to high. This ensures electron-hole pair generation rates are constant through the experiment. Defects are highly temperature sensitive; therefore, if the emission spectrum changes with temperature, this is a quality indicator of defects. In contrast, if the spectrum retains its original features despite the temperature change, then this is an indicator of the absence of defects.

3.6.2 Modeling

Monte Carlo Simulation of Electron Trajectory in Solids, or CASINO v. 2.42, is used to model the electron pathways through the crystal. The program operates by using pseudo-random numbers to approximate statistically significant events. Each electron undergoes a number of collisions, scattering in random trajectories until the electron comes to rest in the material or is backscattered out of the material. Each trajectory is calculated in a stepwise manner with the scattering angle of each collision randomly chosen. Its application here is to determine what energy provides an average depth of penetration necessary for surface excitation. As discussed in the previous section, the narrow $5f^2 \rightarrow 5f^1 6d$ gap and high atomic mass of single crystal UO_2 easily attenuates photons in the visible spectrum. Those photons generated from the luminescence processes discussed in Section 2.7.3 deep within the crystal will not reach the surface, let alone the detector. Therefore, penetrating the crystal with higher energy electrons provide no new information and may unnecessarily cause damage to the crystal.

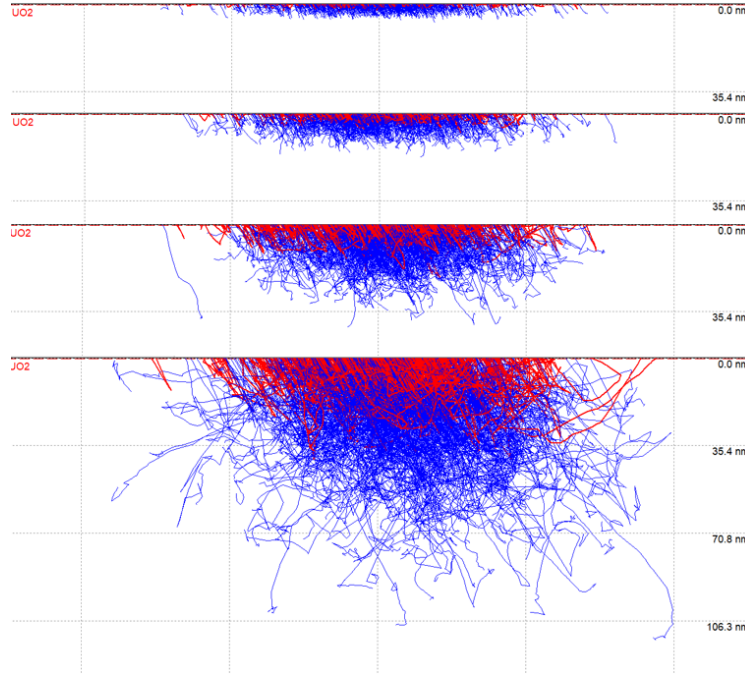


Figure 17. CASINO Simulations of cathodoluminescence using 0.5, 1, 2, and 4 keV electron beam at 30°.

CASINO is used to determine the average depth of penetration for a distribution of beam energies from 0.1 to 10 keV. The simulations for 0.5, 1, 2, and 4 keV electrons are shown in Figure 17. Red lines represent the track of those electrons that backscatter out of the material, while the blue represent those electrons that do not. Each simulation consists of 20,000 electrons using Mott cross-sections and the Joy-Lou modification to the Bethe-Bloch energy-loss equation. The beam width is 100 nm and at an angle of 30° to the 1 mm thick sample. The maximum depth of penetration distribution is then uploaded into MATLAB, where an average penetration depth is calculated as shown in Table 3.

Table 3. Average penetration depth of various beam energies

Beam Energy (keV)	Average Penetration Depth (nm)	Beam Energy (keV)	Average Penetration Depth (nm)
0.1	0.42	1	11.5
0.2	1.47	2	21.6
0.3	2.44	3	47.8
0.4	2.69	4	61.4
0.5	4.44	5	73.2
0.6	5.75	6	102.1
0.7	5.61	7	123.7
0.8	7.59	8	139.7
0.9	7.17	9	178.2
-	-	10	258.0

As to be discussed in more detail in the photoluminescence modeling section, the mean free path of a 34 eV photon in uranium is approximately 13 nm. Data does not exist on the attenuation coefficient of UO_2 in the energy range of the band gap, so a logical assumption is made about the extrapolation of the data to estimate that the mean free path of a 3.4 eV photon is approximately 1.3 nm. This would mean beam energies over 0.2 keV would penetrate the sample too deeply. Higher beam energies would serve to only cause defects on the surface without providing the needed emission spectrum. However, the CASINO simulations are run on stoichiometric UO_2 . Oxidation and native surface defects are not considered in the CASINO simulations. These could potentially reduce the luminescence at such a low power. Therefore, all cathodoluminescence was conducted at a beam energy of 0.5 keV. This ensures a thorough investigation of the surface, regardless of the defects while not introducing unnecessary damage by penetrating too deeply.

3.6.3 System

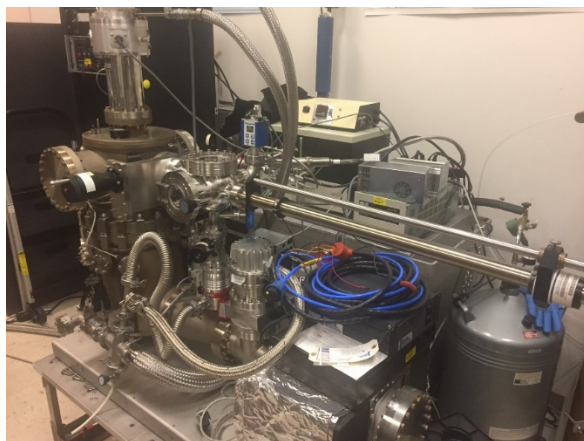


Figure 18. Cathodoluminescence System

The CL system consists of three main components: the main chamber with cooling and vacuum pumping subsystems, the electron gun, and the photon-collecting and analyzing subsystem. The main chamber is a vacuum-sealed stainless steel sphere as shown in Figure 18. The sample holder is located at its center and is coupled with a *Leybold Inc.* CoolPower 4.2 CGM liquid helium cryocooler (cold finger) regulated by a *Lake Shore Cryotronics Inc.* 330 temperature controller. Samples are mounted by tantalum wire spot-welded onto a stainless steel faceplate that is secured to an oxygen-free high-conductivity (OFHC) copper holder. The copper holder is then placed at the end of a manipulator arm and inserted into the nitrogen-flushed load lock where vacuum is reestablished first by a *Varian Vacuum Technologies Inc.* scroll pump to 7.0×10^{-3} Torr and then by a *Pfeiffer Vacuum* turbo pump to 2.5×10^{-7} Torr. Once vacuum in the load lock equalizes with that of the main chamber, the manual gate is opened and the manipulator arm is driven forward inserting the sample into the sample holder in the

center of the chamber. Vacuum in the main chamber is maintained by an *Agilent Scientific Instruments* turbo pump at 10^{-8} Torr. The sample holder faces rearward towards a quartz window with the electron gun facing the sample offset by a 30° angle as depicted in Figure 19.

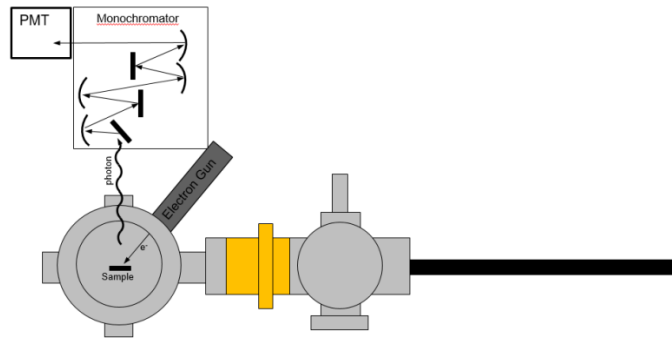


Figure 19. Schematic of Cathodoluminescence main chamber.

The electron gun, shown in Figure 20, is a *Kimball Physics* EMG-12B gun with a barium oxide cathode and tungsten filament. Electrons are created in the cathode, accelerated by an electric field, and focused into a narrow beam by focus tubes and deflector plates. By adjusting the deflector, the location of the beam can be moved to maximize luminescence or to examine structural irregularities at various locations on the crystal face. By adjusting the focus, the beam width can be narrowed or widened. Beam voltage can range from 100 to 20.0 keV. The current can range from 10 nA to 50 μ A.

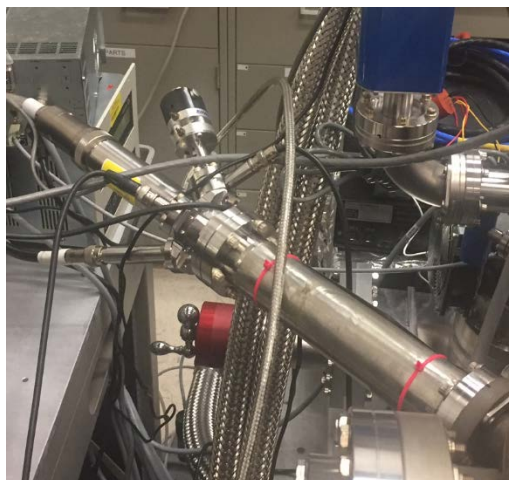


Figure 20. Kimball Physics EMG-12B electron gun

The emitted photons exit the chamber through the quartz window into the ambient air of the laboratory and then pass through a 30 cm planoconvex focal lens whose focal length is the same distance from the sample to the window. The light then passes through a 15 cm planoconvex focal lens whose focal length-to-diameter ratio is precisely that of spectrometer grating. Matching this ratio with the grating helps reduce the signal-to-noise ratio. From the second lens, the light enters a *Horiba Scientific Inc. Spex 500 M* monochromator through a narrow slit, reflects off two mirrors unto a rotatable grating that will alter the wavelength of transmitted light. The light reflects off two more mirrors through another slit and into the *Products For Research Inc.* photomultiplier tube (PMT) where it is collected and analyzed. The PMT is liquid nitrogen cooled to reduce thermionic emission from the photocathode thereby reducing the signal-to-noise ratio. The spectrum is produced with *SynerJY™* by *Horiba Scientific*. It allows for manipulation of the parameters of wavelength range, integration time, and monochromator step size in producing spectra.

3.6.4 Experimental Techniques

With the sample loaded, vacuum established, and chamber and PMT temperature brought down to the desired temperature, the electron gun's high voltage power supply is turned on. The current is slowly raised to 50 μA . Next, the electron gun is opened, directing the electron beam into the chamber. The current should drop to approximately 6 μA . The electron beam is aligned to the desired location on the sample face with the x/y deflector control knobs and adjusted to desired beam width.

When calibrating the monochromator, the program must be set to preview mode and the monochromator set to the wavelength that corresponds to the maximum emission. By placing *SynerJYTM* in continuous run, these three parameters are adjusted until maximum intensity is acquired. With the system calibrated, independent adjustment of the integration time can then be adjusted as desired. A longer integration time results in a greater amount of signal to the PMT but at the expense of experiment time. Wavelength step size can also be adjusted as desired for better resolution, but like integration time, at the expense of experiment time.

With the calibration complete, the system is ready to scan the sample over the desired wavelengths. Each sample was scanned from 2000 to 8000 $\text{\AA}$ at 0.8 second integration time at 1 nm steps. Integration time and step size can be adjusted as needed to either increase detail or reduce collection time. Beam power is set to 1 keV over a width of 100 nm in the center of each sample. The temperature is set to its coldest setting. All spectra are analyzed and peaks are fit using *OriginProTM*.

3.7 Photoluminescence

3.7.1 Theory

PL systems share a number of similarities with CL systems; but fundamentally, the systems differ by means of excitation source. The underlying physics of luminescence is the same. PL excites electrons by means of photons, typically from a lamp or laser. For many PL systems, it is valuable to break the luminescence spectra down into two categories: excitation and emission. In the case for emission, as it is in CL, light is emitted resulting from the de-excitation of electrons back to the valence band. These spectra are recorded by exciting a sample with a fixed-wavelength beam of photons, and any photons emitted from the sample pass through another monochromator that allows the various wavelengths of photons present to be individually recorded by a photomultiplier tube (PMT). With the wavelengths of emission identified (i.e., emission peaks), attention can then be turned to excitation, if so equipped. Here, the wavelength of exciting light is varied across a range of wavelengths. The emitted light passes through a monochromator, which is set to allow only the desired wavelength of emitted light through and into the PMT. The PMT records the intensity of the desired wavelength as a function of the excitation wavelength. This is known as photoluminescence excitation (PLE).

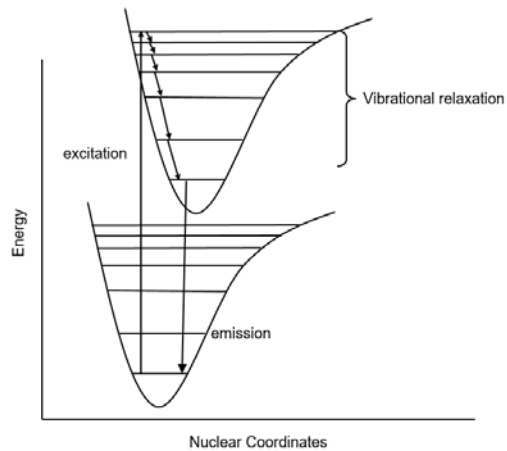


Figure 21. Configuration-Coordinate model depicting Stokes Shift of excitation versus emission energy.

Electrons are excited into the conduction band, both electronically and vibrationally. Within each electronic state there are vibrational states. The vibrational states are the first to relax and do not present luminescence as shown in Figure 21. The electronic state then relaxes by emitting a photon. Because of this energy difference between PL and PLE, as shown in Figure 22, a peak in the emission spectrum is expected to be at a higher wavelength than the same peak from the excitation spectrum. This is known as a Stokes shift. The emission spectrum is usually a mirror image of the excitation peak, shifted to longer wavelengths and at lower intensities. Shown in Figure 22, the excitation and emission spectra of $\text{ThO}_2:\text{Pr}^{3+}$ have a small overlap [69]. The excitation peak at ~ 200 nm creates strong emission at ~ 500 nm, while the excitation peak at ~ 275 nm creates strong emission at ~ 620 nm.

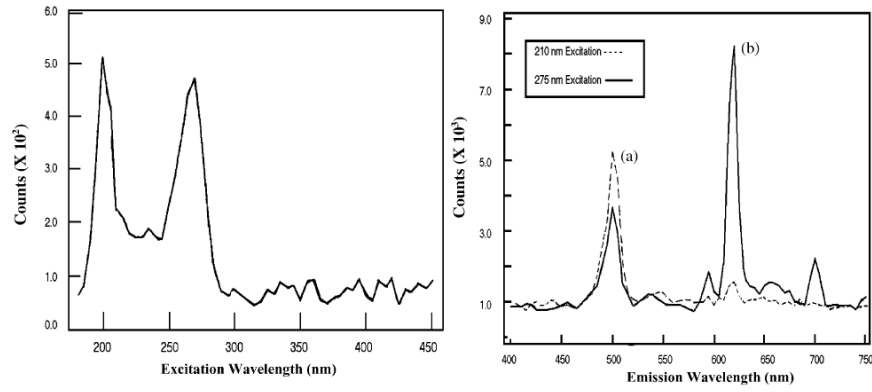


Figure 22. Sample ThO₂ emission and excitation spectra. Figure copied from Godbole *et al.* [69].

3.7.2 Modeling

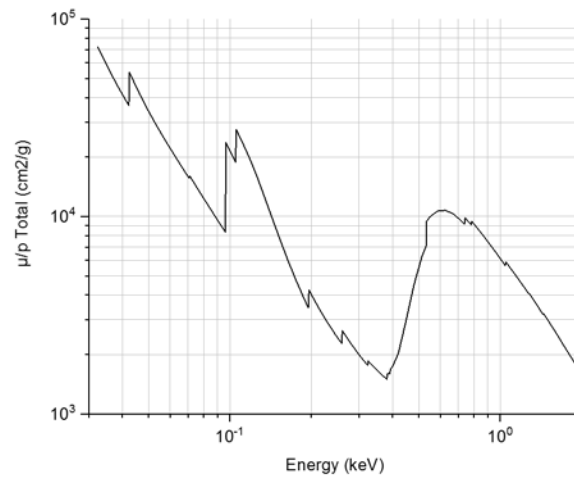


Figure 23. UO₂ Mass Attenuation Coefficient at Low Energy [70].

The attenuation suffered by a beam of photons through a material can be calculated using (12) [71]. Figure 23 depicts the low photon energy mass attenuation coefficients for UO₂.

$$\frac{I}{I_0} = \exp^{-(\mu/\rho * \rho * x)} \quad (12)$$

$$\begin{aligned} I/I_0 &= \text{Percentage of light Attenuated} \\ \mu/\rho &= \text{Material mass attenuation coefficient [cm}^2\text{/g]} \\ \rho &= \text{Material density [g/cm}^3\text{]} \\ x &= \text{Material thickness [cm]} \end{aligned}$$

The data are provided by the National Institute of Standards and Technology.

Unfortunately, the data stop at 32 eV. The mass attenuation coefficient for 38 eV photons, 10x the energy of the 325nm laser, is $6.91 \times 10^4 \text{ cm}^2\text{/g}$ [70]. The density of UO_2 is 10.97 g/cm^3 . Solving (12) for x, when 99% of the photons are attenuated results in a distance of 60.7 nm. This is a back-of-the-envelope calculation for a photon energy 10x higher than what is used in this experiment. It does not consider interactions with surface defects, impurities, and the presence of excess oxygen due to oxidation. However, it can be accurately stated that defect investigation by means of PL is restricted mostly to the surface. Assuming a straight line from the end of the low energy data and extrapolating to 3.8 eV, the attenuation coefficient would most likely be an order of magnitude larger. If this assumption is made and the calculation repeated with $6.91 \times 10^5 \text{ cm}^2\text{/g}$, 99% attenuation would occur at 6.07 nm.

A value of greater importance is found in the exponent of (12). The mean free path of a 38 eV photon in UO_2 is 13.19 nm. Photons emitted below their energy will have a smaller mean free path. Making the same simplistic assumption as above, the mean free path of a 3.8 eV photon is 1.319 nm. This shows that photons generated below the surface by this value will undergo scattering, loose energy, and if collected by the PMT, provide input into the spectrum that can be misinterpreted. This is why such a low electron gun power was chosen for cathodoluminescence.

3.7.3 System

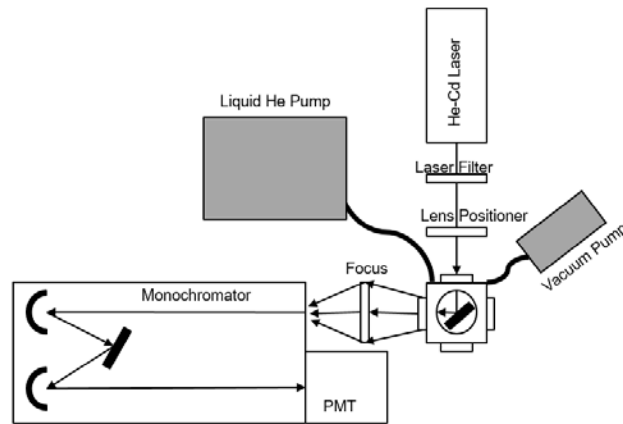


Figure 24. Schematic of Photoluminescence System

As highlighted in Figure 24, the PL system utilizes a *Kimmon Koha Co., LTD.* IK series helium-cadmium (HeCd) 325 nm laser. The laser passes through a *Newport Research Corp.* neutral density laser power filter. It then passes through a *Newport Research Corp.* lens positioner assembly that allows three-axis position adjustment to focus the 80 μm laser beam on the intended target. The sample is vertically mounted to a copper faceplate with rubber cement. The mount is bolted on top of a long vertical stand wrapped in heating coils. A thermocouple is attached to the backside of the mount for temperature reporting. A *Janis Research Co., LLC* chamber is placed over the sample and the mount/stand and securely clamped down. A *Drivac Inc.* turbo pump, controlled by a *Varian Vacuum Technologies Inc.* 880 Vacuum Ionization Gauge controller pulls a 10^{-6} Torr vacuum inside the chamber. A *SHI Cryogenics Group* HC-4E liquid helium pump, controlled by a *Lakeshore Cryotronics Inc.* 331 Temperature Controller, brings the chamber temperature down to 10 K. Any light emitted from the sample passes through a

15 cm planoconvex movable focal lens, through a 345 nm high-pass filter, and into a *Horiba Scientific Inc. SPEX 1250 M* monochromator through an adjustable slit. The light reflects off a series of mirrors unto a rotatable grating that will alter the wavelength of transmitted light. The light reflects off more mirrors through another adjustable slit and into a *Products for Research Inc. PHOTOCOOL™* series photomultiplier tube (PMT) where it is collected and analyzed. The PMT is water cooled to reduce thermionic emission from the photocathode, thereby reducing the signal-to-noise ratio. The spectrum is produced with *SynerJY™* by *Horiba Scientific*. It allows for manipulation of the parameters of wavelength range, integration time, and monochromator step size in producing spectra.

3.7.4 Experiment Techniques

When calibrating the monochromator, a zinc oxide semiconductor wafer is used as this gives off terrific luminescence with well-established peaks. With the system calibrated, the sample is loaded, vacuum established, and temperature brought to the system's coldest temperature, ~ 10 K. The laser is then focused onto the sample producing luminescence. Using the lens positioner, the placement of the beam is adjusted to any area that provides a brilliant luminescence. A quick full spectrum scan will reveal any features present in the sample. The most prominent material-specific peak should be identified. By placing *SynerJY™* in continuous run, the lens' foci, monochromator slit widths, and laser power can be adjusted until maximum intensity is acquired of that particular wavelength.

Monochromator slit widths are adjusted to $\sim 1000\text{ }\mu\text{m}$. Laser power is initially set to 1 mW during the set up, but increased to 5 mW for all spectral runs. Integration time is set to either 0.4, 0.8, or 1.2 seconds, and a step size of either 0.5, 1, 2, or 5 Å. A longer integration time and shorter increments result in a greater amount of signal to the PMT but at the expense of experiment time. The emission wavelength is scanned from 3450 to 6400 Å. At 6500 Å there exists a large peak that represents the second order peak of the laser ($3250\text{ Å} \times 2 = 6500\text{ Å}$). Quick scans did not reveal any obvious features beyond these limits. All spectra were analyzed and peaks fit using *OriginPro*TM.

3.8 Neutron Irradiation

3.8.1 Theory

Neutrons are not readily found outside of the nuclei except as the byproducts of certain nuclear reactions and from certain decaying isotopes. In addition, they are certainly not found in quantities and for periods that are as easily detectable as are the other forms of ionizing radiation. Free neutrons beta decay into protons with a half-life of 10.6 minutes [72]. A solid-state detector made from UO_2 would experience neutron-induced fission. The fission fragments, prompt gamma rays, and prompt neutrons would deposit approximately 180 MeVs of kinetic energy into the surrounding UO_2 crystal lattice creating a large quantity of electron-hole pairs that would produce a large electrical pulse in the device, providing great energy resolution over background.

However, the introduction of a high quantity of fission fragments and their subsequent decay daughters into the crystal lattice may serve to degrade the device's

electronic properties and structural integrity over time by introducing a multitude of new defects. Soullard and Alamo calculated that 26,300 uranium and 76,000 oxygen point defects are created per fission event in UO_2 [73]. Matzke *et al.* gives 1.5×10^4 Frenkel pairs [74]. Both publications do not take into account recombination. Olander surmised that these numbers should be reduced by an order of magnitude to give the most accurate estimate of the point defects produced per fission [75].

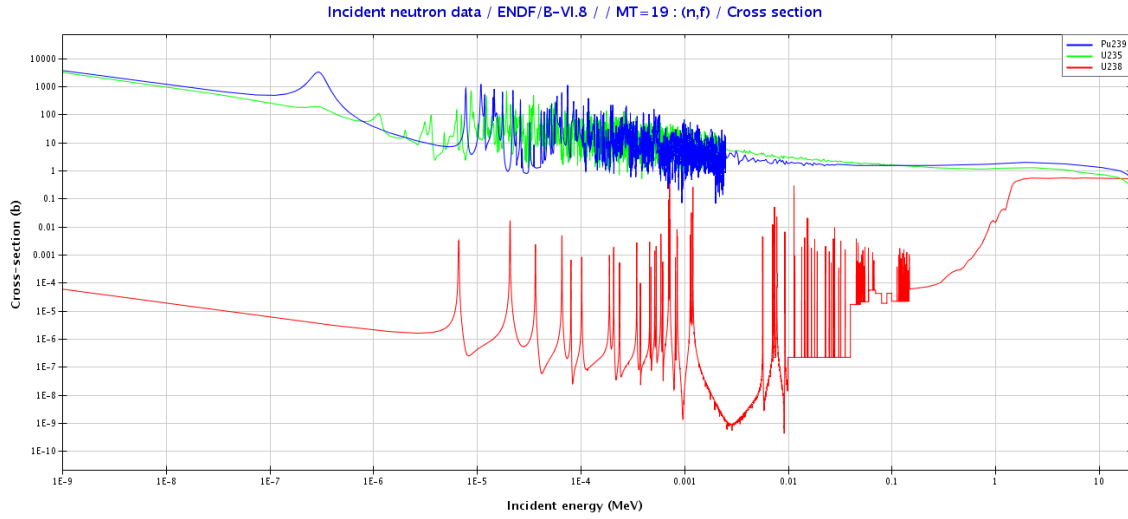
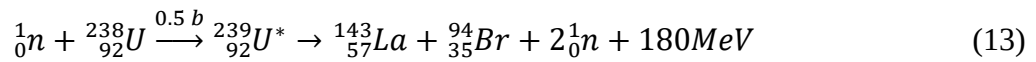


Figure 25. Cross Section of ^{235}U , ^{238}U , and ^{239}Pu plotted against the incident neutron energy provided by the Evaluated Nuclear Data file/B-VII.1[66].

The chief challenge to constructing a device using primarily ^{238}U is its small fission cross section compared to fissile ^{235}U and ^{239}Pu at neutron energies lower than approximately 2 MeV, as depicted in Figure 25. The fission reaction itself is depicted in (13) using one possible result of ^{238}U fissioning from a neutron with energy of 2.45 MeV.



The neutron is absorbed into ^{238}U nuclei temporarily forming a highly unstable ^{239}U nucleus, which immediately leads to the fission into two smaller fragments. At fission,

the nuclei of the fission fragments are also highly unstable and in an elevated energetic state. The nuclei discharge energy to their ground state in the form of a prompt gamma(s) and expel excess neutrons. The reaction energy, depicted as a product in this case, represents the prompt energy released during fission, where 168 MeV comprises the kinetic energy of the two large fission fragments leaving 12 MeV between the prompt neutrons and gammas. These high-energy gammas are distinguishable from lower energy photons emitted from nearby (n, γ) (n,n') reactions and bremsstrahlung x-rays.

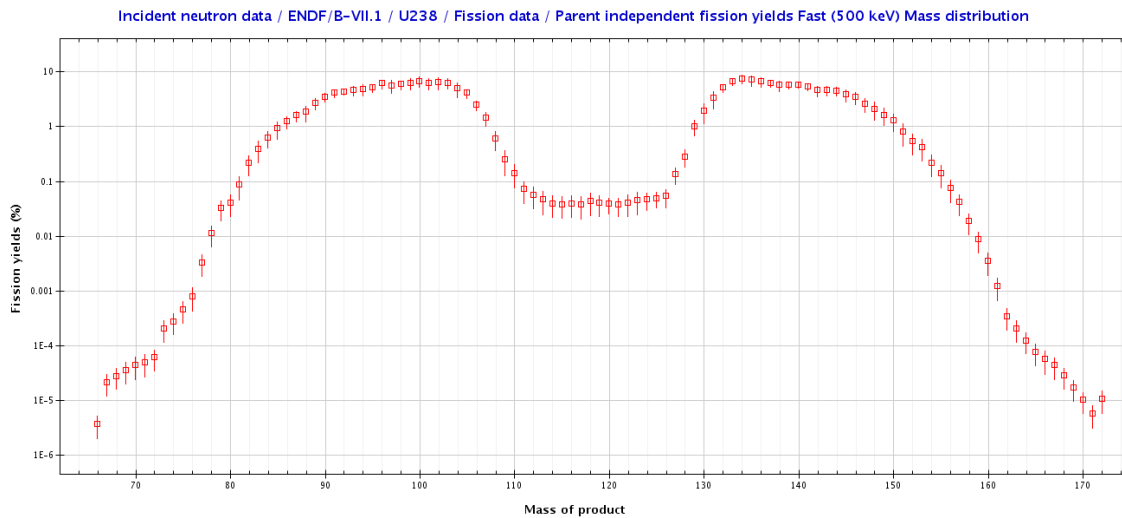


Figure 26. Fission yield of ^{238}U with 500 KeV neutrons provided by the Evaluated Nuclear Data file/B-VII.1 [5].

The actual fission products vary for each fission and can only be statistically predicted based on past observation and theoretical calculations. Figure 26 depicts the statistical distribution of fission fragments based on mass and probability of production from fission of ^{238}U due to a fast neutron. As suggested by the double hump curve in Figure 26, a spectrum of products are produced from fission with certain species and certain mass chains of decay being more probable than others. Table 4 shows the ten

most probable independently yielded isotopes and isobars from fast fission of ^{238}U . Most of the species quickly beta decay into a chain of radiative daughter isotopes of varying activities. Most of the decays do not proceed directly to the energetic nuclear ground state of the daughter product but rather to an elevated energy resulting in gamma-ray emission(s) toward the ground state.

Table 4. Select Fission Isotopic / Mass Chain Yield for ^{238}U Fast Neutron Fission [66]

Isotope	Half Life	Ind. Yield	Cum. Yield	Isobar	Mass Chain
52 Te 135	19.0 (± 2) s	4.62	5.54	134	7.46
38 Sr 96	1.06 (± 3) s	4.13	5.19	135	7.04
40 Zr 102	2.9 (± 2) s	4.09	4.62	133	6.73
54 Xe 140	13.6 (± 1) s	4.04	4.90	100	6.72
40 Zr 101	2.3 (± 1) s	4.00	5.51	136	6.68
52 Te 134	41.8 (± 8) m	3.95	6.85	102	6.45
39 Y 99	1.477 (± 5) s	3.74	4.73	103	6.27
53 I 137	24.51 (± 6) s	3.53	5.13	99	6.24
52 Te 136	17.5 (± 2) s	3.53	3.70	137	6.23
40 Zr 100	7.1 (± 4) s	3.30	6.50	101	6.21

Deciphering the broad gamma-ray spectrum to determine the species initially produced and currently present is best done with a high-resolution detector such as HPGe. With peaks in the spectrum identified and measured for counts, the number of nuclei of any fission product and, ultimately, the total number of fissions, can then be calculated. However, care must be taken to identify and discriminate the gamma-ray spectrum that stems from the various daughters of the natural uranium decay chain.

3.8.2 Modeling

Irradiation of the samples is modeled in MCNP6 and the source code is presented in Appendix A. The neutron source is modeled as an isotropic point source producing 10^9 neutrons per second. $\text{UO}_2\text{-T-93D}$ serves as the model as it is the simplest geometry to

model. Its results are applied to the other two samples as well. The sample is modeled at 0.282 cm from the point source such that the sample is laying length-wise on top of an acrylic stand along the neutron path providing the greatest depth of material for each neutron to pass through. 0.282 cm was chosen due to is simplification of the math. Multiplying the flux by $4\pi(0.282)^2$, which is simply 1 cm^2 , results in the same number only reduced to neutrons per second. This allows for simplified multiplication of the number of fissions per neutron to produce fissions per second. For the actual experiment, the generator housing prevents the sample from being any closer than about 5 cm. The simulation stops after 10^6 neutrons pass through the sample, at which time 161 fissions should have occurred. Multiplying this fission rate by the neutron emission rate through the cross sectional area of the sample at 0.282 cm from the source, a total fission rate of 161,000 fissions per second is calculated. 1.39×10^8 fissions over this period of irradiation are produced. Since the thickness of the sample size is small compared to the MFP of the neutrons, all fissions are assumed to be homogeneously distributed throughout the sample. By taking Olander's assumption of $\sim 10^3$ defects per fission, 24 hours of irradiation should create 1.39×10^{13} defects in each sample.

The gamma dose following irradiation is estimated using the *Dosimetry and Shielding* ++ calculator from www.nucleonica.com. Calculations are made using the number of fissions created above to produce the 34 most prevalent fission fragments as alluded to in Table 5. In addition, a one-hour cool down is assumed and dose is measured 10 cm from the source through air. The resulting tissue gamma dose following the above-described irradiation is 6.14 $\mu\text{Sv/hr}$. Dose estimates for one day and seven days are included in Table 5. The activity following irradiation is estimated using the *Decay*

Engine for Large Nuclide Sets++ calculator from www.nucleonica.com. Utilizing the same mixture and irradiation conditions mentioned above, the estimated activity for the three periods previously mentioned are also shown in Table 5. These calculations ignore the fact that the fissions do not all happen at once but over a 24-hour period. Therefore, the actual activity and dose will be smaller than the numbers provided.

Table 5. Gamma Dose and Activity Calculations

	1 Hour	1 Day	7 Days
Dose	6.14×10^0	$1.01 \times 10^{-1} \mu\text{Sv/hr}$	$1.06 \times 10^{-2} \mu\text{Sv/hr}$
Activity	$4.49 \times 10^5 \text{ Bq}$	$2.021 \times 10^4 \text{ Bq}$	$7.69 \times 10^3 \text{ Bq}$

3.8.3 Neutron Generation System

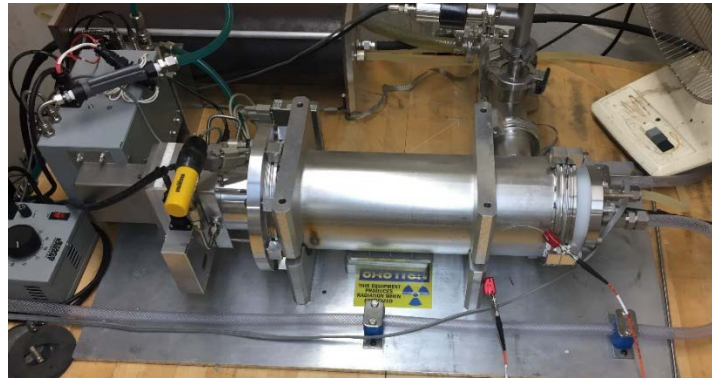
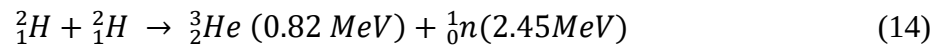


Figure 27. Adelphi Technology DD109 Neutron Generator

The neutron source available for this experiment was an Adelphi Technology DD109 Neutron Generator pictured in Figure 27. Utilizing the deuterium-deuterium (D-D) fusion reaction, the generator produces 2.45 MeV isotropic neutrons as given by (14) [72].



This energy is right on the cusp of ^{238}U 's fission cross section drop off, as shown in Figure 25, and a portion of the neutron flux emitted from the generator would have reduced energies after undergoing scattering. This is reduced by placing the sample close to the source. This reaction is ultimately advantageous as the 2.45 MeV neutrons are more easily moderated than those from deuterium-tritium (D+T) fusion, thereby reducing the shielding requirement. In addition, tritium is radioactive so the safety and maintenance requirements for operating a D+T generator is considerably more burdensome than a D+D generator.

3.8.4 Experimental Techniques

With the system operating as per the department's operating instruction, the samples are stacked one atop of the other and placed at 8.46 cm in front of the source (30x 0.282 cm). This theoretically should produce a fission rate 30x less than what was modeled. A Geiger counter with a Bonner Sphere is placed in the room to provide auditory confirmation that the generator is working. The room is locked and the generator is turned on and operated for 24 hours. Following irradiation, the samples were loaded into a lead crucible and transported to the HPGe detector. Each sample is then loaded into its own HPGe detector for a 24-hour spectrum that then can be compared to its original. The difference between the two will be the fission products created and their decay daughters.

IV. Analysis and Results

4.1 Overview

This chapter presents the data collected, provides the requisite analysis for answering the established research questions backed by published literature, and provides theories as to the unanswered questions. The chapter is broken down into four main sections. First, the results of XRF and Gamma Spectroscopy are presented to provide a baseline understanding of foreign impurities present in the sample prior to conducting the optical measurements. Next, the PL results are discussed in detail. CL data is unfortunately absent due to technical difficulties that prevented any data from being taken. Therefore, along with the PL measurements being conducted at AFRL, neutron irradiation also was not accomplished. This chapter is concluded with a summary of the data and a look at how the investigative questions were answered.

4.2 Pre-Irradiation Measurements

4.2.1 XRF

Investigating elemental composition through XRF showed all but one face of the three samples were primarily uranium, ranging from 78.39% to 92.04%. The beta face of UO₂-T-93B was primarily thorium with only one spot of the 9-point raster scan showing a significant amount of uranium at 39.47%. This was obvious observing the face as it was noticeably opaque, characteristic of ThO₂, overlaying a black sublayer. This is certainly from the seed crystal. When 93B was cut from the seed crystal, the cut line must have

been deeper into the U/Th transition layer leaving a majority thorium face. Two of the decay daughters of ^{238}U are thorium isotopes. However, this could not be the cause of this thorium layer. It would not only have shown up in one of the five other faces if so, but also the half-lives are such that the amount observed could not have accumulated in the time span following crystal growth. In fact, all five had thorium present in <3% and 93D contained no thorium at all. 93B's beta side was further polished to remove this thorium layer to prevent stress cracking at cryogenic temperatures. The combined nine spectra from each sample face are shown in Appendix B. Only those peaks of uranium and thorium are labeled.

Each sample had a host of other elements present; many at concentrations of <1%. Many of these elemental impurities were only present in certain spots of the raster scan. Many of the elements identified are transition and rare earth (RE) metals. 93B's alpha side had significant amounts (> 2%) of germanium, zirconium, and tungsten in multiple locations. 93B's beta side had little to none of these three elements. In fact, the beta side was dominated by an excessive amount (> 25%) of magnesium in addition to the Th. 93D's alpha side contained significant amounts (> 2%) of aluminum, scandium, zirconium, and cesium, but only in one or two locations. It also contained significant amounts of gadolinium and astatine in multiple locations. 93D's beta side contained excess amounts of silicon in addition to significant amounts of magnesium, potassium, nickel, zirconium, palladium, platinum, gold, and astatine in multiple locations. 93E's alpha side contained significant amounts of magnesium (only one location), germanium, bromine, terbium (only one location), lutetium, tungsten (only one location), and radon. The beta side also had a considerably lower uranium percentage thanks to significant

amounts of nickel, gallium, platinum, astatine, and thorium in multiple locations. Spot 1 had significant amounts of aluminum, silicon, potassium, copper, zinc, and gallium not present in the other locations. Appendix B shows the full elemental break down for each sample face. These impurities are most likely the results of contamination of the feedstock, the mineralizer, and/or contamination from the technicians during setup.

Decay daughters of uranium were present, but in low quantities. Francium was present above 1% in two of the six sample faces. That is a possible indicator of the presence of ^{235}U as it is the fourth decay daughter of ^{235}U with a short half-life of 22 minutes. Rhodium was present in each of the scans as expected based on the XRF description in Section 3.4.1. Table 6 presents a brief overview of the elemental makeup of the samples. Only those elements present in quantities above 1% in at least one sample are considered. For more fidelity on what is present, Rhodium is excluded from Table 6.

Table 6. Overview of element makeup ($\geq 1\%$) of each sample face.

93B (α)		Mg	Ge	As	Zr	Pd	I	Gd	Lu	W	Hg	Rn	Fr	Ra	U
	Maximum	0.62	4.80	0.26	3.34	2.00	1.04	1.20	2.16	5.40	1.16	3.09	1.23	1.47	91.95
	Minimum	0.62	0.27	0.26	0.91	2.00	0.31	1.20	0.14	0.15	0.15	0.24	0.20	0.05	79.59
93B (β)		Mg	Al	Si	S	Ge	Rb	Tc	Sn	Cs	At	Rn	Th	U	
	Maximum	33.01	5.45	4.04	1.67	2.18	1.87	1.02	2.47	2.45	1.29	1.07	81.38	39.47	
	Minimum	8.63	0.52	0.23	0.41	2.18	1.16	0.68	2.47	0.78	0.39	0.23	13.18	0.01	
93D (α)		Al	K	Sc	Cu	Zr	Pd	Cs	Gd	Hg	Tl	At	U		
	Maximum	7.70	1.42	4.13	1.74	2.76	1.51	4.95	2.18	3.06	3.27	4.26	92.48		
	Minimum	7.70	1.42	4.13	0.03	1.13	1.51	0.80	1.26	3.06	0.78	2.37	78.39		
93D (β)		Mg	Al	Si	K	Ni	Y	Zr	Pd	Pr	Lu	Pt	Au	At	U
	Maximum	6.65	1.86	47.50	3.86	9.87	1.04	2.59	2.22	0.14	1.79	2.22	3.61	2.98	78.27
	Minimum	2.90	1.86	8.67	2.56	0.40	0.37	0.73	0.71	0.12	1.48	1.14	0.25	1.41	40.63
93E (α)		Mg	Ge	Br	Zr	Tb	Lu	W	Au	Hg	Rn	Fr	U		
	Maximum	6.12	6.27	3.22	2.80	5.01	2.63	5.63	5.33	4.39	3.17	1.26	92.04		
	Minimum	6.12	0.55	0.72	0.09	5.01	1.05	0.12	5.33	4.39	0.19	0.05	83.80		
93E (β)		Al	Si	K	Ni	Cu	Zn	Ga	Y	Pd	Yb	Pt	At	Th	U
	Maximum	6.01	9.24	2.28	15.47	2.00	6.19	3.61	1.77	3.07	9.98	4.36	3.22	2.88	80.39
	Minimum	6.01	0.28	2.28	3.26	0.01	0.01	1.90	0.42	1.50	5.17	1.18	2.52	0.09	47.96

4.2.2 Gamma Spectroscopy

Figure 28 shows the 8 hour HPGe spectrum of 10 grams of UO_2 powder. As expected, based on the theoretical UO_2 spectrum from Section 3.5.2, this spectrum is dominated by lower energy emission below 100 keV with the large $^{234}\text{Pa-m}$ peak at 1001.02 keV (0.83%). The percentage in parenthesis represents the emission probability of that gamma per decay. The ^{235}U 185.715 keV (57.1%), ^{214}Bi 768.36 (4.9%) keV, and the ^{214}Pb 786.1 keV (0.3 %) peaks are also clearly present. Some of the later decay daughters either have extremely low emission probabilities associated with each gamma energy, or their emissions are below 100 keV and the peak is lost in its contribution to the large broad peak at ~95keV.

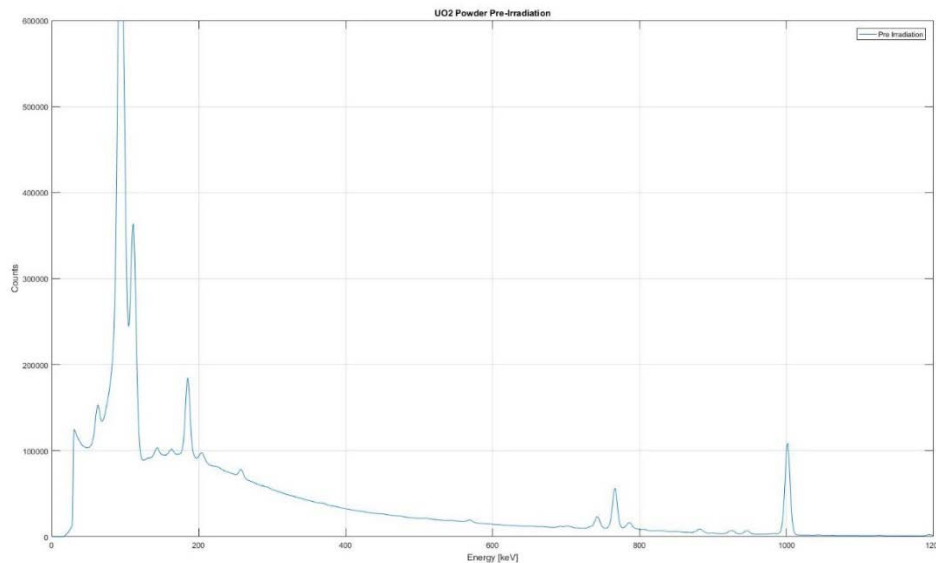


Figure 28. UO_2 (10 g) 8 hour HPGe spectrum

With this experimental knowledge along with the theoretical spectrum to guide the analysis, the spectra for the samples can now effectively be analyzed. Figure 29 depicts the 24 hour HPGe spectrum for each sample overlaid on one another. Two things

quickly stand out. First, 93B produced more counts for each emission. This is to be expected, as 93B was double the mass of the next smallest sample. Secondly, 93B had many additional large peaks that are not present in the other two. XRF scans showed extremely high levels of thorium on one side. This is most likely a result from the cut being too deep into the uranium/thorium transition layer. Comparing peaks from the ^{232}Th decay chain and considering all possible gamma emission proves this true. Table 7 highlights many of these large peaks by identifying the ^{232}Th decay daughter(s) and their emission energy and decay rate. Not all of the ^{232}Th peaks present in 93B are shown in Table 7, as many of the peaks are the result of two or more isotopes emitting in such close energy proximity that discrimination is too difficult.

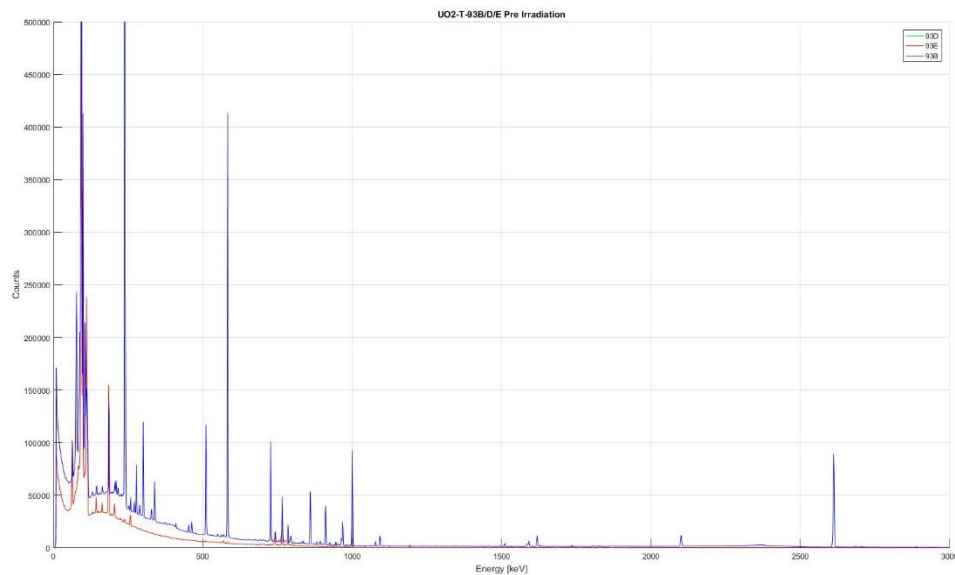


Figure 29. UO₂-T-93 B, D, and E 24-hour HPGe Spectra

Table 7. ^{232}Th decay daughters present in $\text{UO}_2\text{-T-93B}$ HPGe Spectrum

Peak	Nuclide	Energy [keV]	γ Emission Probability [%]	Peak Area	FWHM	Max Height	Peak Center
1	^{212}Pb	238.632	43.5	4085634.956	2.308	1.321E6	238.525
2	$^{208}\text{Tl} / ^{228}\text{Ac}$	510.77	22.8	178.988	2.220	1.145E5	510.420
3	$^{208}\text{Tl} / ^{228}\text{Ac}$	583.191	85.1	3018147.244	2.226	4.273E5	582.744
4	$^{212}\text{Bi} / ^{228}\text{Ac}$	727.33	6.74	233.515	2.292	9.354E4	726.691
5	^{208}Tl	860.566	12.52	126546.376	2.311	5.115E4	859.633
6	^{208}Tl	2614.55	99.83	918893.999	3.905	8.88E5	2611.685

Aside from those peaks that indicate the presence of ^{235}U , ^{232}Th , and its daughters, no other discernible peaks are present that would indicate additional radiative isotopes were present. The presence of cesium had not been anticipated for its part as the mineralizer agent since ^{133}Cs is stable, ^{134}Cs and ^{137}Cs are fission products and the ^{238}U spontaneous fission rate is extremely low, and ^{135}Cs has no associated gamma emission. Many of the ^{238}U decay daughters are not identifiable as their emission probabilities are either too low or their emission energies place them in the large broad peak below 100 keV. Little is known about the UO_2 feedstock other than it comes from an Italian firm. It is most likely spent fuel from a reactor that has been purified to some degree. The feedstock was also measured and a 24 hour spectrum gathered to help identify any impurities in it that might be contributing to the impurities in the crystal. That spectrum is shown in Figure 30. No other discernible radioactive isotopes are present, especially from the ^{232}Th decay chain. This fact eliminates the only other possible sources of ^{232}Th , other than the seed crystal.

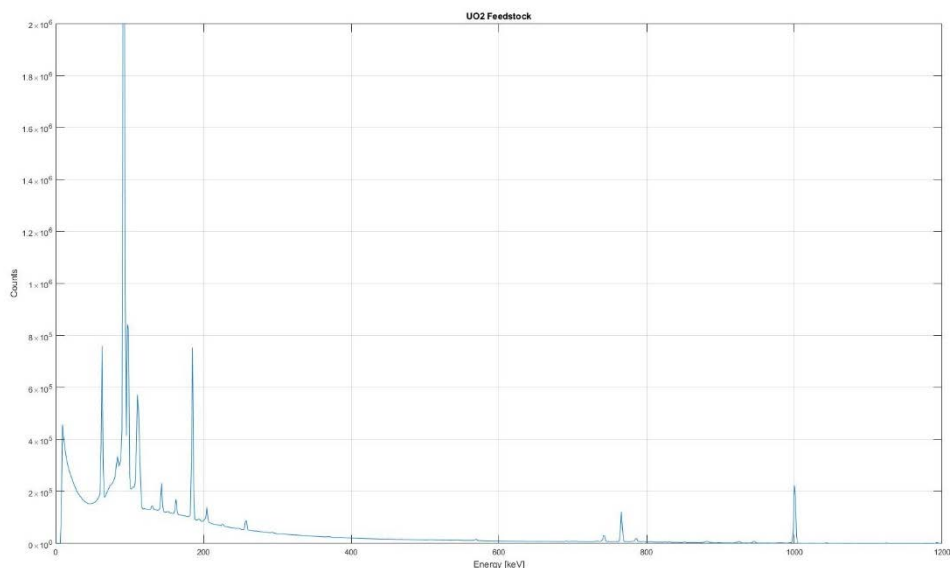


Figure 30. 24-Hour HPGe Spectrum of UO₂ Feedstock

UO₂-T-93 B was polished by the crystallographers to remove the thorium layer on the beta side. When using cryogenics for PL and CL measurements, the lattice mismatch between thorium and uranium, approximately 2.1%, would have been accentuated at low temperatures and would most likely lead to breaking. In addition, each of the three samples broke to some degree from handling during PL measurements. Table 8 highlights the mass changes following the samples breaking during handling. Each of the three samples' 24 hour HPGe spectra were retaken and are present together in Figure 31 below. No ²³²Th and daughters are present. Each sample perfectly mirrors the other two except for the mass differences.

Table 8. Sample mass changes prior to PL measurements

Sample	Weight Before (g)	Weight After (g)	Difference (%)
93B	0.6512	0.2179	-0.4333 (66.54)
93D	0.3640	0.2770	-0.087 (23.90)
93E	0.1994	0.1877	-0.0117 (5.87)

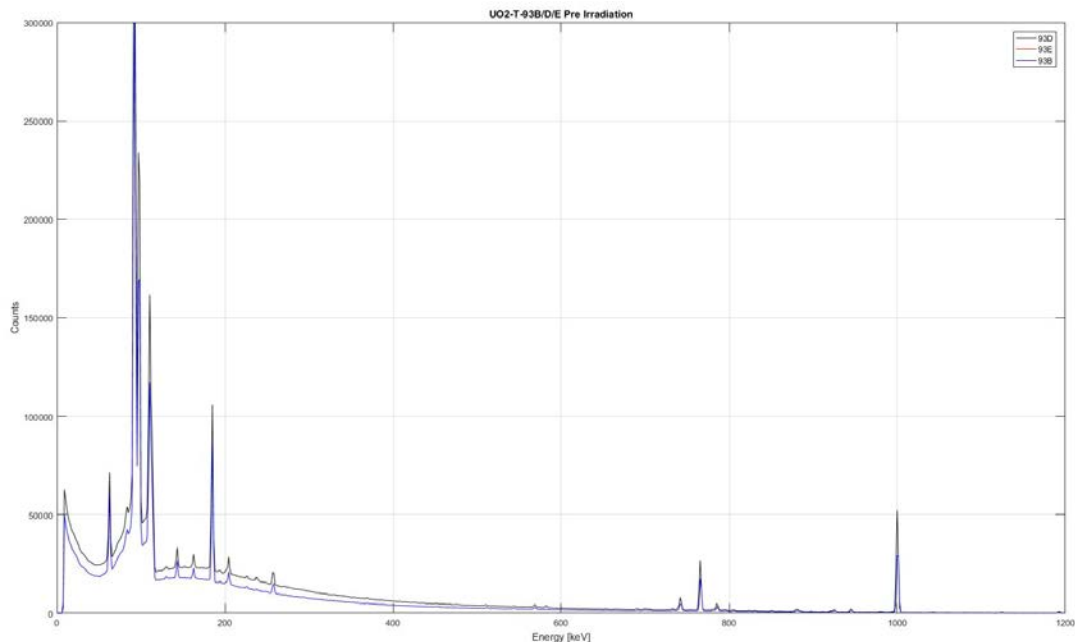


Figure 31. UO₂-T-93 B, D, and E 24-hour HPGe Spectra (after being re-weighed)

Lastly, the ^{235}U 185.715 keV (57.1%) peak was used to approximate the amount of ^{235}U present in the sample. First, the efficiency curve of the HPGe detector had to be established. From the 24 hour spectrum taken on the calibration sample T-175 (1-Nov-16), the number of counts measured for each of the twelve isotopes were compared to the expected count quantity (reported activity $\times$ 24 hours) to produce an efficiency for each isotope. These were plotted as a function of energy and from the curve an equation was fitted using a MATLAB application. Next, the energy of the 185.715 keV gamma was used to calculate the absolute efficiency at that energy through the equation. The amount of ^{235}U decays is calculated by dividing the amount actually detected in 93D by the calculated absolute efficiency. However, the total decays are merely this number divided by the emission probability, 57.1%. Next, the activity was calculated by dividing the total

decays in 24 hours. With the activity in hand, the total number of atoms and weight were calculated to be 1.50×10^{18} and 5.84×10^{-4} grams respectively.

As this uranium is assumed to be made from spent fuel or nuclear enrichment tails, it makes sense to assume that the quantity of ^{235}U is below the 0.7% average of natural uranium. Knowing the quantity relative to ^{238}U and ^{235}U alters the irradiation modeling and could provide for better fission results. One approach would be to ignore all other elements other than ^{238}U and O. However, as discussed in the theory section, UO_2 readily oxidizes and it is unknown at this point to what extent higher oxygen content extends into this crystal. In addition, based on the above HPGe and XRF results, there are small amounts of impurities present. Therefore, the ^{238}U quantity is determined from the HPGe results as follows. Sticking with 93D, $^{234}\text{Pa-m}$ is first analyzed as it is solely responsible for the nicely resolved peak at 1001.02 keV and it happens to be the only second decay daughter of ^{238}U . Each of these two decays occur without any known branching. The $^{234}\text{Pa-m}$ peak at 1001.02 keV (0.83%) is used similarly to how the ^{235}U quantity is calculated. The activity is 1.11×10^7 decays/sec. In order to calculate the amount of ^{238}U present, a major assumption has to be made. For the sake of calculation, it was assumed that the $^{234}\text{Pa-m}$ is in secular equilibrium with its parent. It takes 0.96 years (352.12 days) to reach this point from an initially pure ^{238}U sample as depicted in Figure 32. Therefore, if the activity of $^{234}\text{Pa-m}$ is known, the activity of ^{238}U is known. With this assumption, the quantity and mass of ^{238}U is 6.2929×10^{20} atoms and is 0.2488 g respectively. This means that the 235/238 ratio is 0.24%, well below natural uranium.

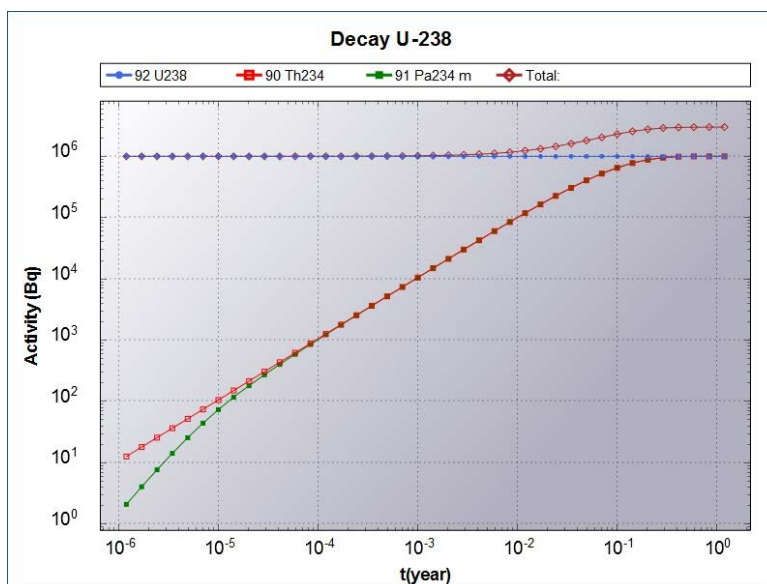


Figure 32. ^{238}U decay and daughter product activity as a function of time.

0.2488 g of uranium from a 0.2770 g sample is 89.8% by weight. However, uranium in stoichiometric UO_2 is 88.1% by weight. With increased oxidization, as expected with these samples, the uranium percentage should be lower. These calculations are highly sensitive to the number of counts under the full energy peak. Manually counting the area under the full energy peak instead of extracting using software that fits a normal distribution to the peak, renders a higher count by 3.96%, resulting in a 5% increase of uranium in the sample. These calculations are based on an efficiency curve that was generated from a standard multinuclide source with an uncertainty of 3.1% across all energy levels. This error then serves as the baseline for the overall calculation error, and is most likely higher than this. This level of error accounts for the calculation discrepancy. In addition, $^{234}\text{Pa-m}$ has another gamma emission at 995 keV (0.004%) that could be influencing these numbers. Despite these potential influencers, the quantities of uranium calculated for 93D are reasonable, given the many unknowns about the sample.

4.2.3 Photoluminescence

A number of spectra were taken on each sample at various locations across the alpha (uranium) surface. These locations were chosen based upon how the surface appeared and by the luminescence intensity. Areas that offered brighter luminescence were investigated. 93B offered the best luminescence that is characteristic of $5f^16d^1 \rightarrow 5f^2$ transitions in UO_2 , followed by 93D. Since all spectra were taken prior to having a thorough understanding of $5f^16d^1 \rightarrow 5f^2$ and uranyl emission, all spectra were initially deemed faulty or erroneous. With each seemingly erroneous spectrum, the spectrum collection techniques changed to speed up collection in an effort to find a spectrum similar to literature representation of UO_2 having a band gap of approximately 2 eV. Hence, each spectrum's integration time, step size, and wavelength window varied. It is only after the spectra were collected that the literature detailing $5f^16d^1 \rightarrow 5f^2$ and uranyl emission was considered. Had this knowledge been known ahead of time, collection methodology would have been uniform throughout.

$5f^16d^1 \rightarrow 5f^2$ Transition Luminescence Spectral Analysis

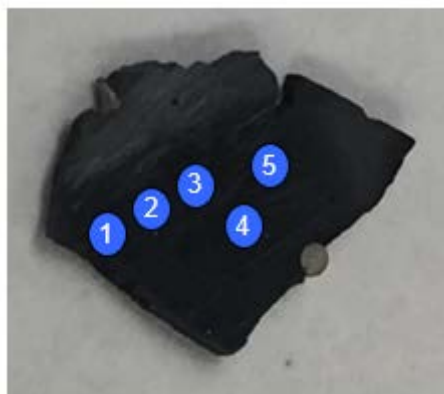


Figure 33. 93B PL spectra spot locations

Five principle spectra were obtained from 93B. The first spectrum was taken at a location nearest to the far right edge as the observer looks at the sample as displayed in Figure 33. This site was logically chosen as the starting point to allow for a sweep of the sample along the longitudinal axis as shown. The exact spot was chosen because this spot was smooth and polished to the naked eye. Spot 1's spectrum was taken at 0.8 seconds integration time, in 5 Å steps, 1000 μm monochromator slit width, and at 9.0 K. The spectrum produced 12 peaks, shown in Figure 34, that are peak-fit such that the peaks are highlighted in green. The spectrum's peak fit R^2 value is 0.9956. The emission from $5f^16d^1 \rightarrow 5f^2$ transitions are anticipated to be highly vibrational-coupled (highly defective crystal structure). In addition, the anticipated uranyl emission is, by definition, vibrational in nature. Therefore, all spectra peaks were fit using Lorentzian functions. The exact peak center of gravity, or where the peak maximum falls on the x-axis, the full width at half maximum (FWHM), and peak area for each peak is detailed in Appendix C.

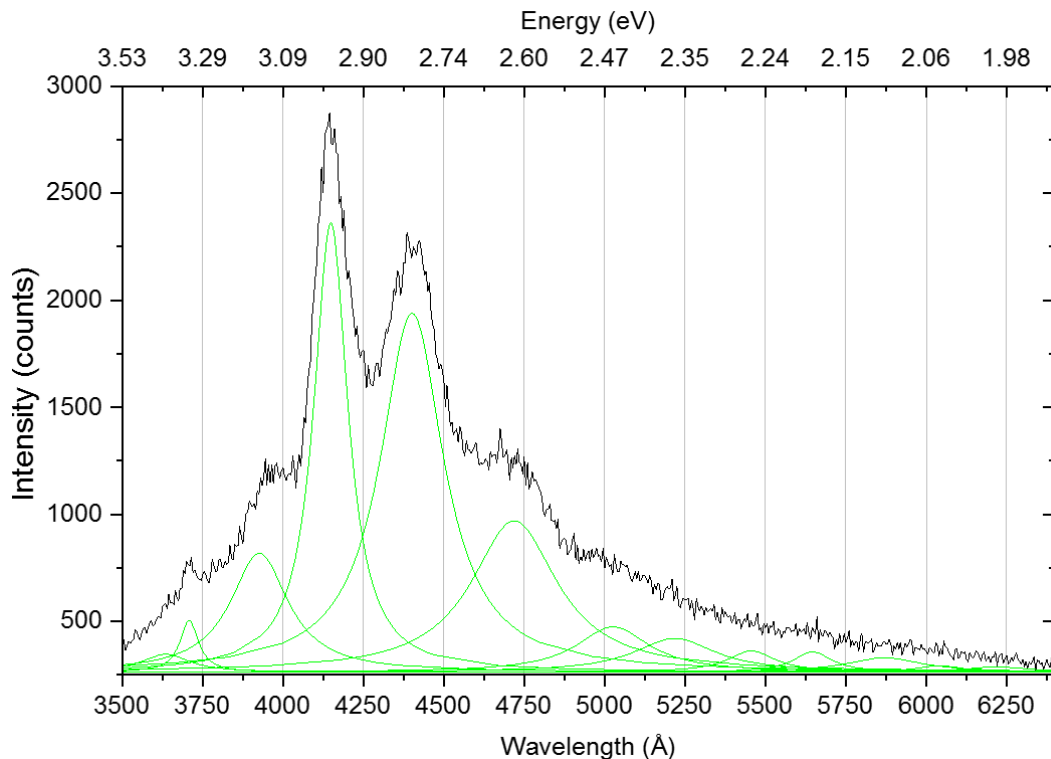


Figure 34. 93B PL spectrum at spot 1 (0.8s integration. time, 5 Å step size, 325nm excitation at 5mW, and 9.0 K).

As discussed in Section 2.7.4, literature values for the emission of the U^{4+} ion in solution are four intense peaks at 319, 335, 410, and 525 nm, and eight weaker peaks at 289, 292, 313, 321, 339, 346, 394, and 447 nm. As evident in the spectrum, four peaks at 3926.3, 4148.6, 4401.1, and 5218.4 Å match extremely well with the literature values. However, a critical issue arises from this comparison. Kirishima *et al.* credits these wavelengths to $5f \rightarrow 5f$ transitions. Their transitions are highly resolved peaks (i.e., small FWHM). The peaks presented above are intense relative to the overall spectrum and broad – both characteristics of $5f^1 6d^1 \rightarrow 5f^2$ transitions. Other important points to consider are that the 3926.3, 4401.1, and 5218.4 Å peaks do not match Kirishima *et al.*'s intensities, and the other peaks are not present in Kirishima *et al.*'s study. This leads to

the conclusion that this spectrum, if representative of $5f^16d^1 \rightarrow 5f^2$ UO_2 emission, provides these values for the first time. It just so happens that three transitions share similar energy values to the $5f \rightarrow 5f$ transition of U^{4+} in perchlorate solution.

Another important factor to consider from relevant literature is that the highest energy transition, $5f^16d^1 (e_g) ({}^2F_{5/2}) \rightarrow 5f^2 ({}^3H_4)$, does not necessarily produce the most intense emission peak. Kirikova *et al.*'s study on $\text{LiYF}_4:\text{U}^{4+}$ showed that this transition, the largest in terms of energy, is in fact the most intense peak in their emission spectrum at 257 nm [54]. However, Godbole *et al.* performed a similar study on the same compound and found this transition was not the most intense, but rather the $5f^16d^1(e_g) ({}^2F_{5/2}) \rightarrow 5f^2 ({}^3F_2)$ [53]. In fact, Godbole *et al.*'s emission spectrum, shown in Figure 35, looks similar to 93B's spot 1 spectrum, albeit shifted to lower wavelengths.

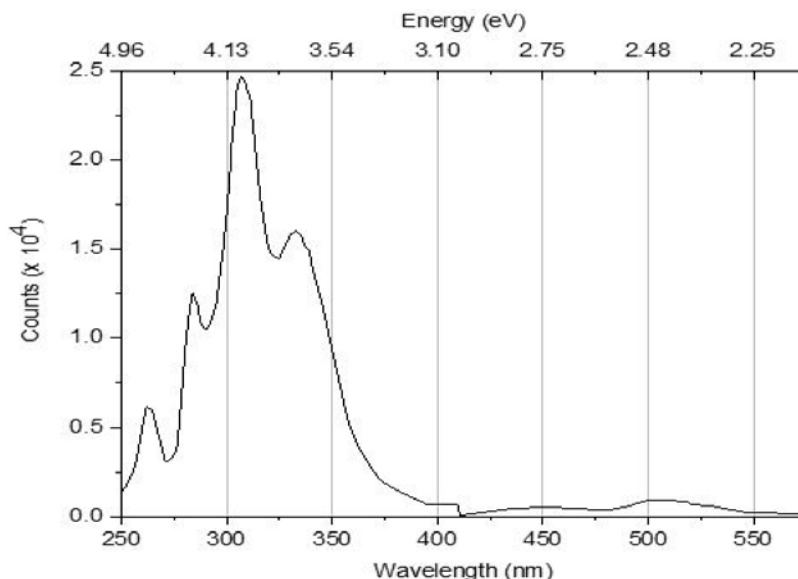


Figure 35. Emission spectra of $\text{LiYF}_4:\text{U}^{4+}$ by Godbole *et al.* [53]. Adapted using a plot digitizer from <http://digitizer.sourceforge.net/>.

Additionally, based on the uranyl discussion in the next section, the 4719.0, 5026.1, 5218.4, and 5456.3 Å peaks may also be candidates for uranyl emission. This is

possible as the surface of the samples are expected to have some degree of oxidation based on the discussion in Section 2.6. Any possible uranyl emission from samples discussed in this section will be explored further in the next.

Spot 2's spectrum was also taken at 0.8 seconds integration time, 5 Å steps, 1000 µm monochromator slit width, and at 9.0 K. The spectrum produced 12 peaks, shown in Figure 36, that are peak fit such that the peaks are highlighted in green. The spectrum's peak fit R^2 value is 0.9949.

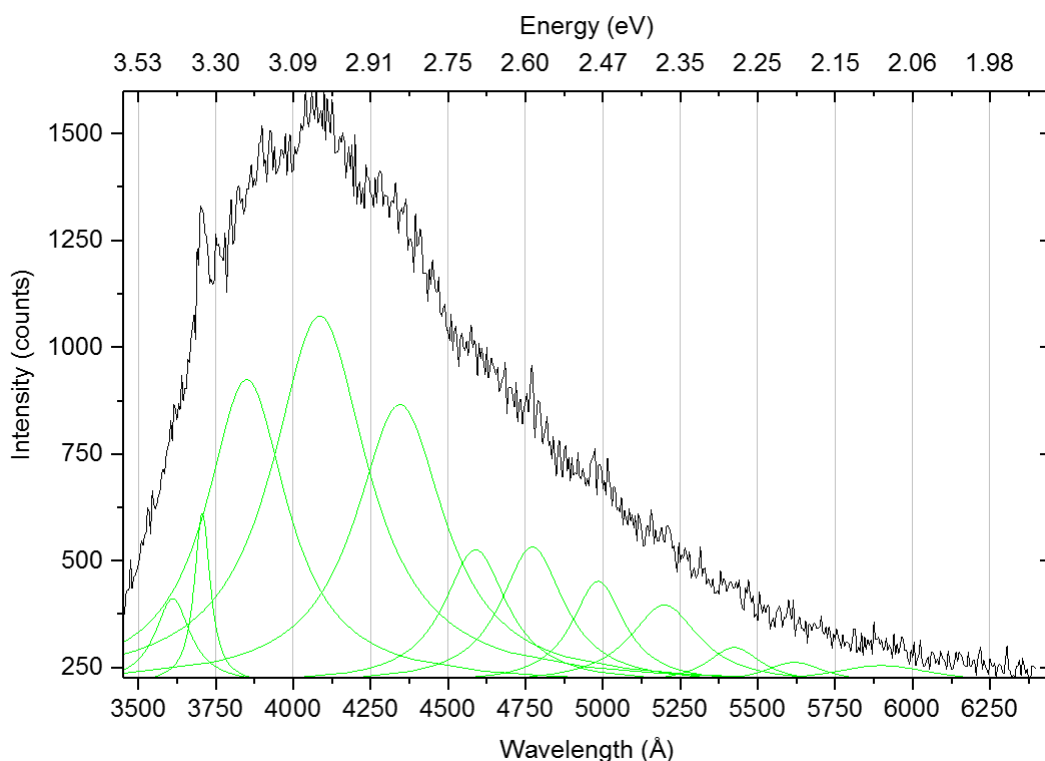


Figure 36. 93B PL spectrum at spot 2 (0.8s integration time, 5 Å step size, 325nm excitation at 5mW, and at 8.7 K).

The peaks in this spectrum are not as well resolved as the peaks in the previous spectrum. This may be an indication of increased vibrational coupling due to crystal defects at this location. All but peak 6 is in good agreement with spot 1's spectrum,

except for the increased intensities of peaks 3 and 5 through 9. The peak at 4588.9 Å does not have a counterpart in any of the five spectra taken from 93B presented in this section. Unlike spot 1, spot 2 does not have peaks at 6034.1 ± 9.9 and 6213.5 ± 9.6 Å. However, if the spectrum had been taken at 1 Å steps with 1 second integration time, these higher wavelength peaks may be present.

Spot 5's spectrum produced results similar to spot 2 and is, therefore, presented ahead of spot 3 and 4. This spectrum was expected, as the surface of spot 5 was smooth and polished like 1 and 2. Spot 5's integration time was held at 0.8 seconds and 5 Å step size to keep collection time short. The monochromator slit width was 1000 µm and temperature was at 9.1 K. Shown in Figure 37, the fitted peaks are highlighted in green. The spectrum's peak fit R^2 value is 0.9694. All peaks are consistent with spots 1 and 2 except the 4588.9 Å peak in spot 2 is missing and a peak at 5798.9 Å is present in spot 5 that was not in spots 1 and 2. The relative intensities match closely with those in spot 2.

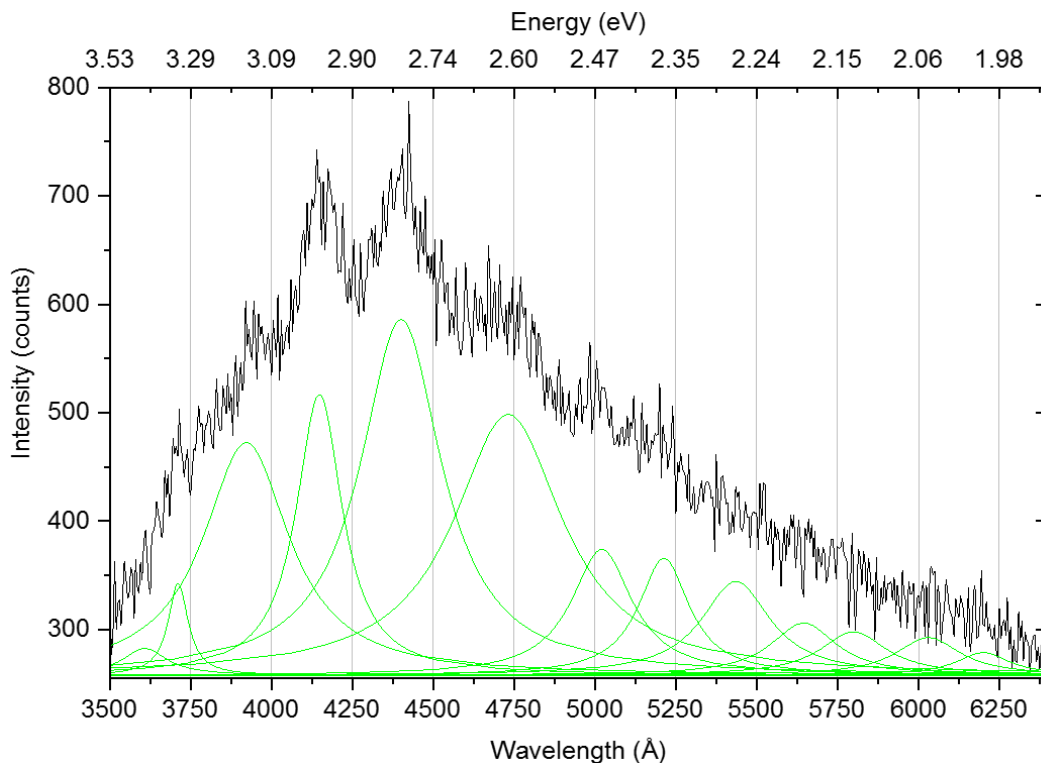


Figure 37. 93B PL spectrum at spot 5 (0.8s integration time, 5 Å step size, 325nm excitation at 5mW, and at 9.1 K).

In each of these three spectra, a peak at 3708.8 ± 1.9 Å is present. This peak is much more highly resolved than their peers, especially in spot 2's spectrum. This is unlikely to be a $5f \rightarrow 5f$ transition as these transitions are much less intense than are their $5f^1 6d^1 \rightarrow 5f^2$ counterparts. If the 3639.3 ± 21.0 Å peak does represent the largest of the $5f^1 6d^1 \rightarrow 5f^2$ transitions, the $5f^1 6d^1(e_g) (^2F_{5/2}) \rightarrow 5f^2 (^3H_4)$ representing the bottom of the conduction band to the ground state of the $5f^2$ band, then the 3708.8 ± 1.9 Å peak may represent a defect lying just below the conduction band; as it is right below the conduction band, at liquid helium temperature, and highly resolved. This may also be some form of exciton transition. This peak could also represent an extrinsic donor. Before a defect is assigned to this peak, the remaining spectra were explored.

Spot 3's spectrum was taken in what appeared to be a discolored region of the sample face, as shown in Figure 38. The resulting emission spectrum was anticipated to be different as this is a possible site of oxidation.

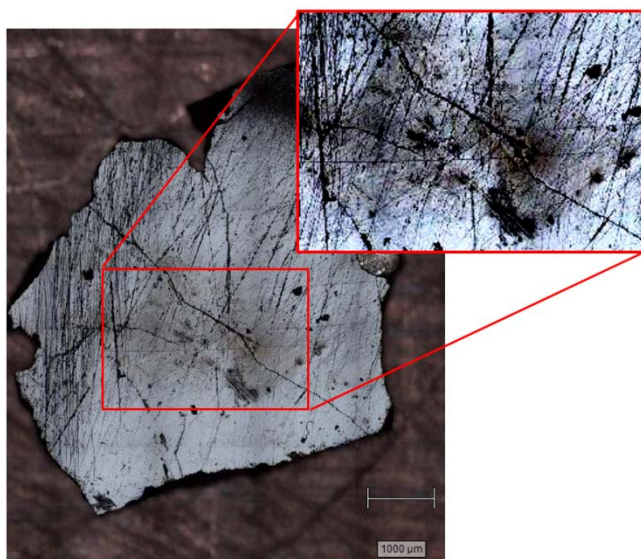


Figure 38. Visible light microscope picture of 93B isolated, and magnified where the spectra for spots 3 and 4 were taken. Contrast altered to highlight discoloration.

To capture the most detail from the spectrum, the spectrum was taken at 2 seconds integration time and 1 Å steps. The monochromator slit width was 2000 μm and temperature was at 9.2 K. The spectrum is a large broad peak with a maximum around 3900 Å that decays toward higher wavelengths. This peak is peak-fit in a similar fashion to the previous three with the peaks highlighted in green as shown in Figure 39. At the summit, ten additional well-resolved peaks appear to occur at regular intervals. These peaks are highlighted in blue and are analyzed later in this section and referred to as “spectrum peaks”. The spectrum’s peak fit R^2 value is 0.9978.

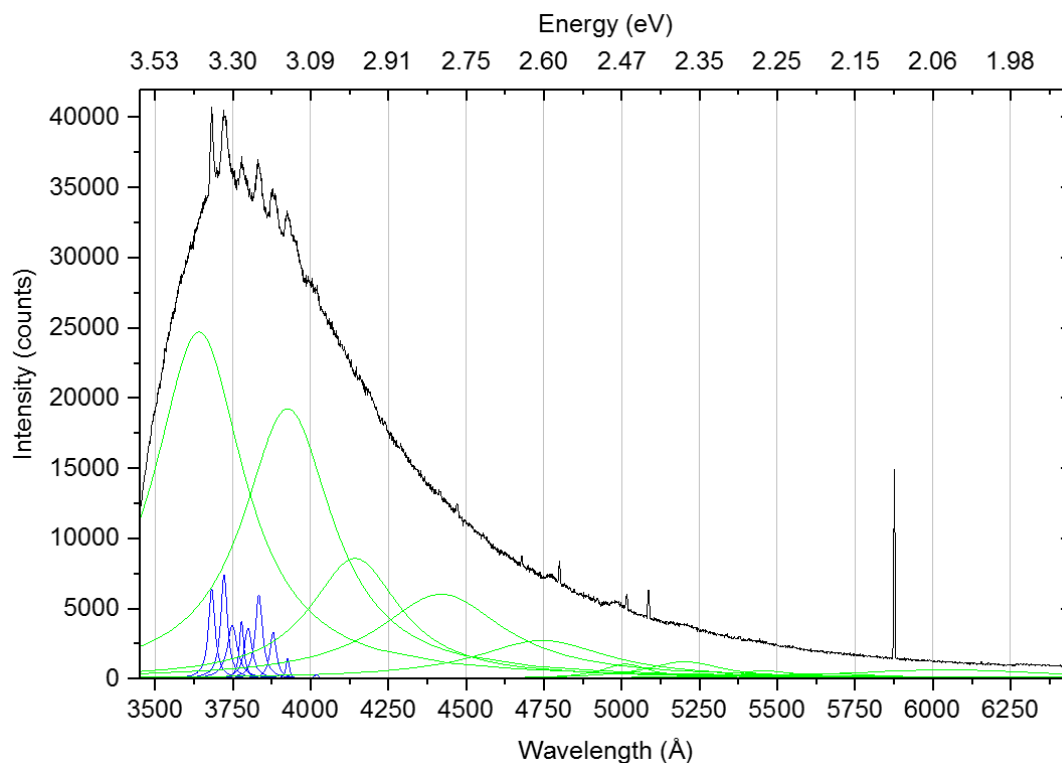


Figure 39. 93B PL spectrum at spot 3 (2s integration. time, 1 Å step size, 325nm excitation at 5mW, and at 9.2 K).

With no apparent peaks except those highly resolved peaks at the summit, peaks were fit manually using both literature values and the previous spectra as a starting point. These peaks are mostly consistent with spots 1, 2, and 5, except for the absence of the 3708.8 ± 1.9 , 5452.1 ± 17.2 , 5635.4 ± 9.9 , 6034.1 ± 9.9 , and 6213.5 ± 9.6 Å peaks. In addition, there is a peak at 6044.4 Å. Peaks 5 through 8 are candidates for uranyl emission as well. Unlike the previous spectra, five sharply resolved peaks appear between 4500 and 6000 Å. These lines are the 5015 and 5875 Å spectral lines of helium and the 4678, 4799, and 5085 Å spectral lines of cadmium that are a result of the reflection of the laser off the

surface and into the monochromator. This follows as this sample is polished and the surface smoother than the other samples, even in the discolored region.

Not only is this region discolored, indicating possible oxidation, its surface is also highly defective from apparent scratches left from the polishing process as shown in Figure 38. This is likely the cause of the largest peaks having a greater FWHM than the previous spectra. With the first peaks especially, the FWHM approximately doubles from spots 1, 2, and 5. The intensity significantly increases to where the first peak at 3641.4 Å is now the largest. This increase in both FWHM and intensity is the reason for the loss of clarity between peaks at lower wavelengths producing one large broad peak center at approximately 3900 Å.

Spot 4 deviated from the longitudinal axis to remain in the discolored region for a second spectrum to compare to spot 3. Spot 4's integration time was decreased to 1.2 seconds and step size increased to 2 Å to reduce collection time. Just like spot 3, this spectrum produced a broad main peak around 3900 Å that decays toward higher wavelengths. Peak fitting is highlighted in green in Figure 40. In addition, at peak summit, eight additional well-resolved peaks appear to occur at regular intervals. These peaks are highlighted in blue. The spectrum's peak fit R^2 value is 0.9964. The same spectral lines from spot 3 are present in spot 4. Just like spot 3's spectrum, there is no 3708.8 ± 1.9 Å peak. In terms of peak center-of-gravity, the remainder of the spectrum is most consistent with spot 5 except for the presence of the 5900.0 Å peak, which is consistent with spots 1 and 2. In terms of FWHM and intensity, spot 4 is most consistent with spot 3, as expected due to its location in the discolored and scratched region.

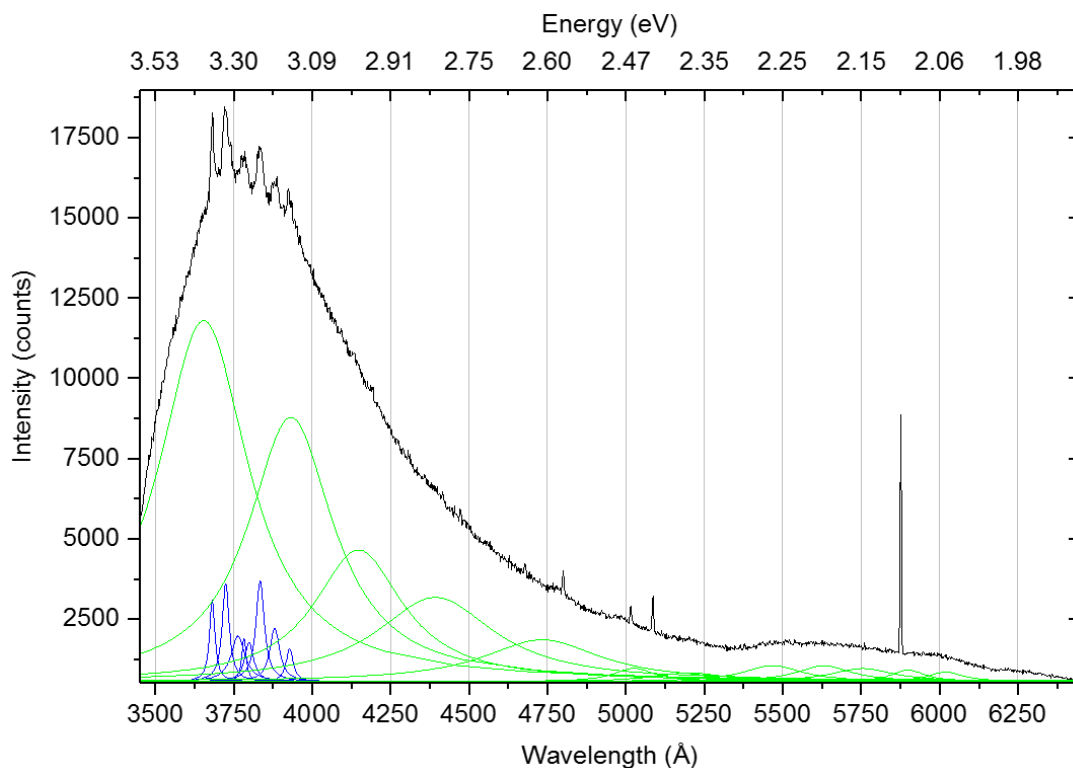


Figure 40. 93B PL spectrum at spot 4 (1.2s integration time, 2 Å step size, 325nm excitation. at 5mW, and at 9.1 K).

Unlike spot 3, the higher wavelength peaks were more intense producing a discernible broad peak extending over approximately 1000 Å. Hashem *et al.* assigned highly resolved emission peaks from U^{4+} in compounds in the 400 to 800 nm range to $5f \rightarrow 5f$ transitions [58]. However, unlike their work, these individual peaks are broad. It is unlikely that these peaks represent something different from the other spectra, as the peaks' center-of-gravity is consistent with the other spectra.

Two principle spectra were taken on 93D. Unlike on 93B, these two spots were selected by randomly searching the crystal surface for the brightest luminescence. 93D did not have any smooth and polished areas, and, therefore, all blue luminescence was

much dimmer. The two spots are shown in Figure 41. 93D did not have the noticeable discolorations of 93B, but it did have two clearly identifiable dark lines intersecting each other across the surface. This sample had been previously loaded into the CL system with the electron gun interacting with the surface for approximately five minutes before the electron gun malfunctioned. The lines are where the tantalum wires crossed over and shielded the surface from the electrons. Because of the bombardment with electrons, even for a short period, the emission spectra were anticipated to be different from 93B spots 1, 2, and 5. Furthermore, sample 93D had also been exposed to a xenon lamp at atmospheric pressure and room temperature in early attempts to conduct PL measurements with a fluorospectrometer. These two previous measurements may have impacted the onset of surface oxidation, and likely are the reason that this sample appears to contain outliers.



Figure 41. 93D PL measurement spot locations

Spot 1's spectrum looks remarkably similar to 93B's spot 3 and 4, albeit with more noise due to the collection methodology. Here a large broad peak is present with a maximum around 3900 Å that decays toward higher wavelengths. The 5875 Å spectral line of helium is again present. Spot 1 was collected with 0.8 second integration time, 5 Å

step size, a 2000 μm monochromator slit width, and at 10 K. Shown in Figure 42, the fitted peaks are highlighted in green. The spectrum's peak fit R^2 value is 0.9997.

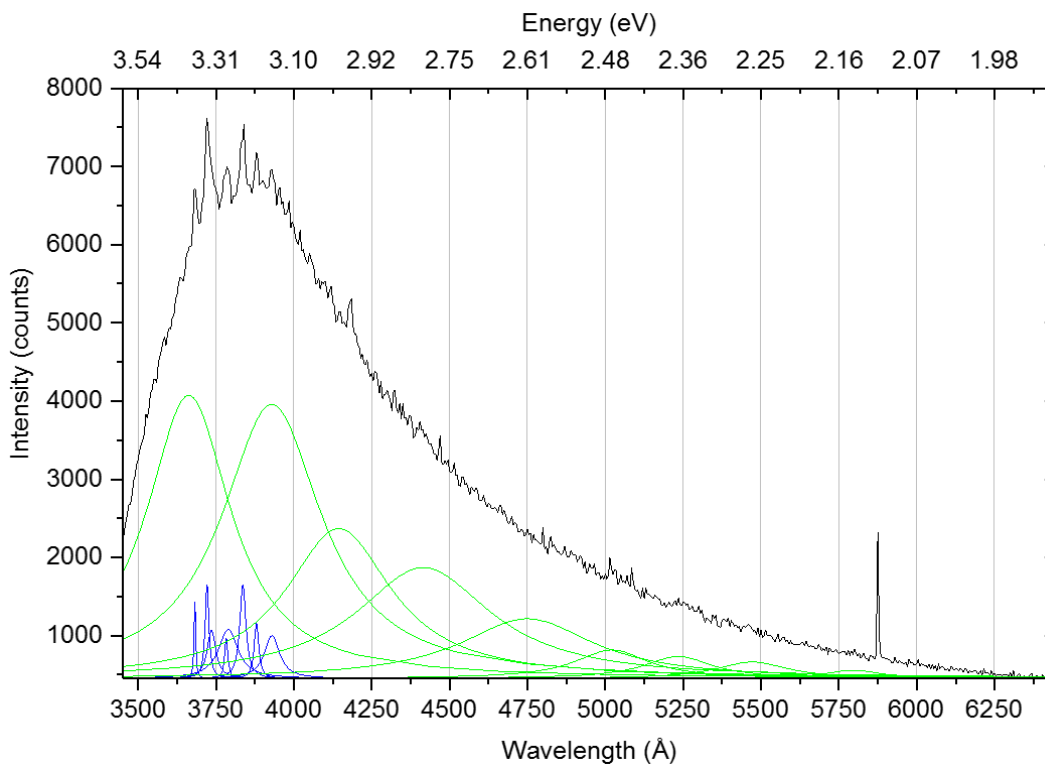


Figure 42. 93D PL spectrum at spot 1 (0.8s integration time, 5 Å step size, 325nm excitation at 5mW, and at 10 K).

The peaks in spot 1 are mostly consistent with all of 93B's spectra. The $3708.8 \pm 1.9 \text{ Å}$ peak that was present in 93B spots 1, 2, and 5 is missing. In addition, 93D spot 1 is missing a peak at $5635.4 \pm 9.9 \text{ Å}$ that is present in all five of 93B spectra. 93D spot 1 also has a 5796.3 Å peak consistent only with 93B's spot 4 and 5. Peak FWHM and area are most consistent with 93B spots 3 and 4 as anticipated.

Spot 2's spectrum was collected with 1.2 seconds integration time and 2 Å step size, a 2000 μm monochromator slit width, and at 10K. Shown in Figure 43, the fitted

peaks are highlighted in green. The spectrum's peak fit R^2 value is 0.9988. Spot 2's spectrum is nearly identical to spot 1's spectrum except for the absence of the helium spectral line. In addition, a peak at 5632.6 Å is present and in agreement with all five of 93B's spectra, and the 5796.3 Å peak in spot 1 is now absent.

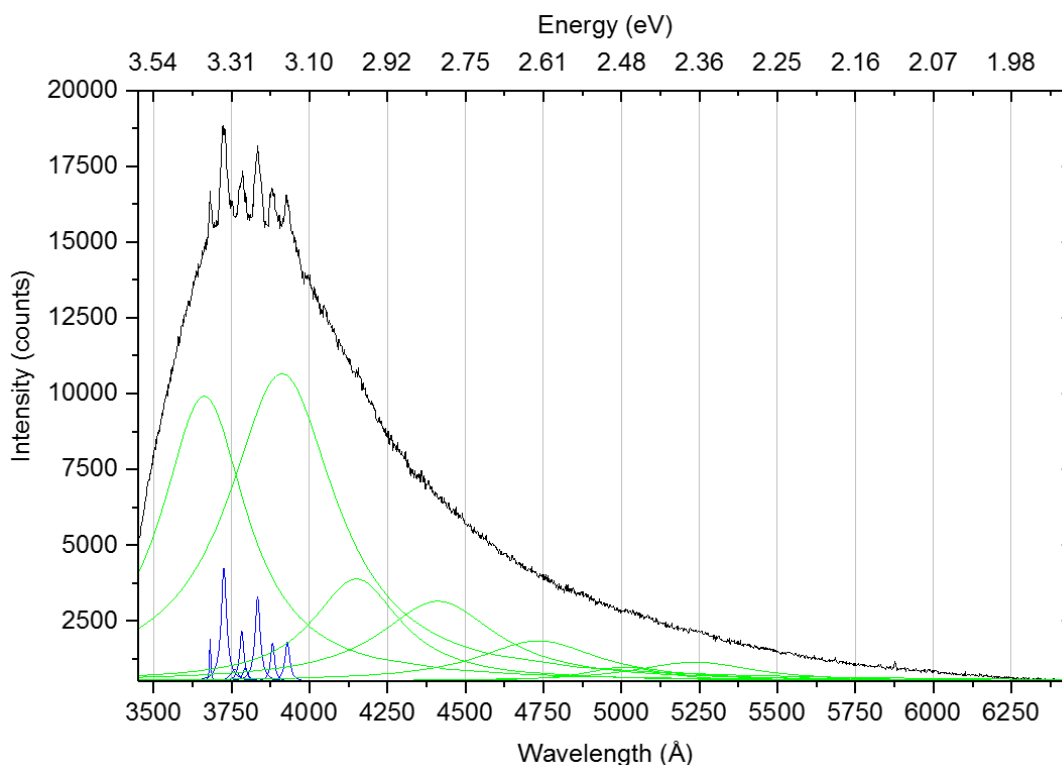


Figure 43. 93D PL spectrum at spot 2 (1.2s integration time, 2 Å step size, 325nm excitation. at 5mW, and at 10 K).

All seven spectra are presented in Table 9 for easy comparison. Each spot is present from left to right, with each peak next to its corresponding peak in each spectrum. For the spectrum that does not contain a certain peak, the spot is left blank. Each peak is averaged over the seven spectra and shown along with its standard deviation. Except for

the 3708.8 ± 1.9 Å peak, the first four peaks have the greatest variability in terms of their center-of-gravity.

Table 9. All U⁴⁺ emission peaks

Peak	93B Spot 1 Peak Center (Å)	93B Spot 2 Peak Center (Å)	93B Spot 3 Peak Center (Å)	93B Spot 4 Peak Center (Å)	93B Spot 5 Peak Center (Å)	93D Spot 1 Peak Center (Å)	93D Spot 2 Peak Center (Å)	Average (Å)
A	3635.2	3610.9	3641.4	3654.3	3608.3	3662.8	3662.4	3639.3 ± 21.0
B	3708.3	3706.7	-	-	3711.3	-	-	3708.8 ± 1.9
C	3926.3	3850.3	3926.3	3932.4	3921.9	3929.3	3911.8	3914.0 ± 26.7
D	4148.6	4086.2	4143.1	4147.8	4147.8	4144.4	4150.3	4138.3 ± 21.4
E	4401.1	4344.9	4420.4	4392.8	4400.4	4416.1	4411.6	4398.2 ± 23.5
F	-	4588.9	-	-	-	-	-	4588.9 ± 0.0
G	4719.0	4772.4	4744.6	4733.1	4731.6	4749.2	4733.4	4740.5 ± 15.8
H	5026.1	4984.9	5012.9	5025.8	5020.9	5020.8	5010.1	5014.5 ± 13.3
I	5218.4	5198.9	5203.6	5202.7	5213.1	5234.1	5234.1	5215.0 ± 13.6
J	5456.3	5423.8	5456.6	5468.3	5435.5	5471.9	-	5452.1 ± 17.2
K	5646.6	5617.3	5639.4	5631.6	5645.0	-	5632.6	5635.4 ± 9.9
L	-	-	-	5755.3	5798.9	5796.3	-	5783.5 ± 20.0
M	5870.7	5899.8	-	5900.0	-	-	-	5890.2 ± 13.8
N	6042.0	-	6044.4	6019.8	6030.1	-	-	6034.1 ± 9.9
O	6217.8	-	-	6222.5	6200.2	-	-	6213.5 ± 9.6

Since the PL system incorporated a 345 nm high-pass filter to remove any of the 325 nm laser light, it is entirely possible that lower wavelength transitions were also filtered out of the spectrum. Most of the reference literature indicates that the more energetic $5f^16d^1 \rightarrow 5f^2$ transitions fall between 250 to 400 nm, which is medium dependent. Without an absorption spectrum to compare to, assigning transitions to these wavelengths is speculative. However, using Godbole *et al.*, Hashem *et al.*, and Kirikova *et al.*'s transition assignments as a guide, the following transitions are cautiously and tentatively assigned to the peaks [53] [58] [54] in Table 10.

Table 10. Assigned $5f^16d^1 \rightarrow 5f^2$ transitions to emission spectra peaks

Emission Wavelength (Å)	Emission Wavenumber (cm ⁻¹)	Energy (eV)	$5f^16d^1 \rightarrow 5f^2$ Transition
3639.3 ± 21.0	27478.5 ± 159.2	3.41 ± 0.02	$^3F_2 \rightarrow ^3H_4$
3914.0 ± 26.7	25550.2 ± 176.7	3.17 ± 0.02	$^3F_2 \rightarrow ^3H_4$
4138.3 ± 21.4	24165.1 ± 126.3	3.00 ± 0.02	$^3F_2 \rightarrow ^3F_2$
4398.2 ± 23.5	22737.3 ± 122.6	2.82 ± 0.02	$^3F_2 \rightarrow ^3H_5$
4740.5 ± 15.8	21095.2 ± 70.3	2.61 ± 0.01	$^3F_2 \rightarrow ^3F_3$
5014.5 ± 13.3	19942.3 ± 53.1	2.47 ± 0.01	$^3F_2 \rightarrow ^3F_4$
5215.0 ± 13.6	19175.6 ± 49.8	2.38 ± 0.01	$^3F_2 \rightarrow ^3H_6$
5452.1 ± 17.5	18341.9 ± 57.9	2.27 ± 0.01	$^3F_2 \rightarrow ^1G_4$
5635.4 ± 9.9	17745.0 ± 31.1	2.20 ± 0.00	$^3F_2 \rightarrow ^3D_2$
5783.5 ± 20.0	17290.8 ± 59.8	2.14 ± 0.01	$^3F_2 \rightarrow ^3P_0$
5890.2 ± 13.8	16977.5 ± 39.7	2.10 ± 0.00	$^3F_2 \rightarrow ^3P_1$
6034.1 ± 9.9	16572.6 ± 27.1	2.05 ± 0.00	$^3F_2 \rightarrow ^1I_6$
6213.5 ± 9.6	16094.0 ± 24.9	1.99 ± 0.00	$^3F_2 \rightarrow ^3P_2$

Godbole *et al.* assigned their first two peaks at the $5f^16d^1 (^3F_2) \rightarrow 5f^2 (^3H_4)$. Their rationale was that the large crystal field splitting in the $^3H_4$ ground state resulted in a spread of about 2700 cm⁻¹. Carnall *et al.*'s work on UF₄ showed a spread of about 1800 cm⁻¹ [76]. The spread in the present work is 1928.3 cm⁻¹. Recall that 93B's spot 1, 2, and 5 spectra had the most well defined peaks at the five lowest wavelengths, excluding the 3708.8 ± 1.8 Å peak. These peaks were present in the other spectra as well. Therefore, these transitions are the most certain. Peaks 5014.5 ± 13.3 Å and above are less certain for two reasons. First, there exists the possibility some of these peaks may be the result of uranyl emission to be explored further in the next section. Secondly, the higher wavelength peaks are not all present in each of the seven spectra, whereas the first five peaks, excluding the 3708.8 ± 1.8 Å, are present in all. Lastly, assigning transitions without the aid of additional information carries much uncertainty regardless of the certainty in peak fitting. Kirikova *et al.* identified one peak as the mixture of emission from $5f^16d^1 \rightarrow 5f^2 (^3F_3)$ and $5f^16d^1 \rightarrow 5f^2 (^1G_4)$. Before any of these transition assignments

can be confirmed, emission data at lower wavelengths must first be collected to rule out peaks in the ~ 3000 Å wavelength that are present in many other studies. In addition, DFT calculations would be vital at not only confirming these transitions, but also confirming that the emission peaks are in fact from $5f^16d^1 \rightarrow 5f^2$ transitions. Modifying both Figures 6 and 34 with the data present in Table 10 in mind, the first five transitions and their energies are shown in Figure 44.

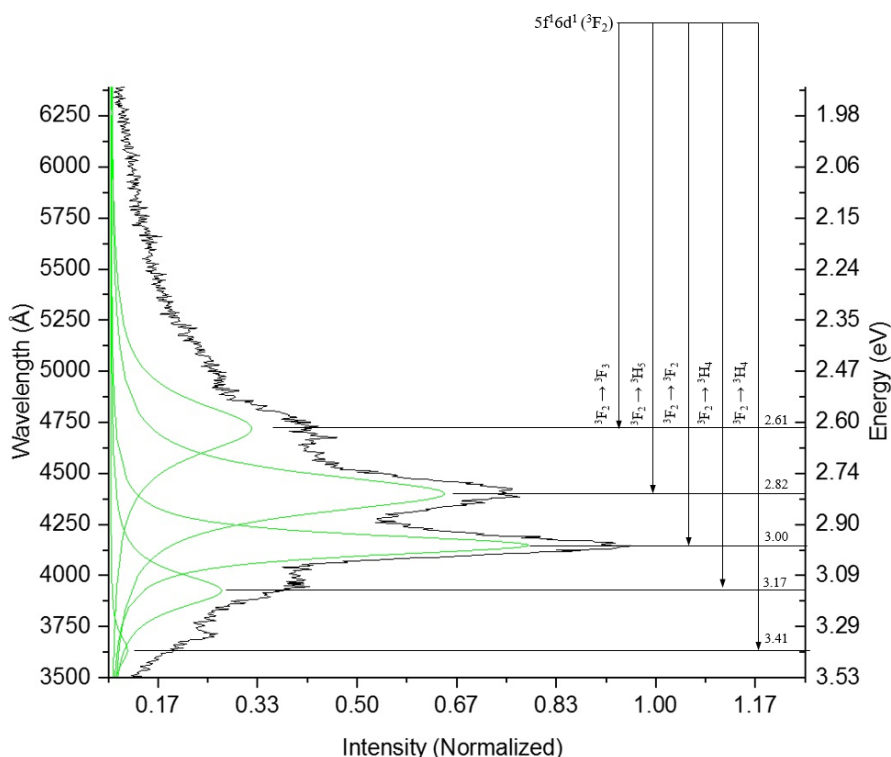


Figure 44. Assigned $5f^16d^1 ({}^3F_2) \rightarrow 5f^2$ transitions depicted on 93B spot 1 spectrum.

In 93B spot 3's spectrum, Figure 39, the peaks highlighted in blue occur in regular intervals of approximately 30 meV. The first peak is the most intense and the most resolved. In the three other spectra (Figures 40, 42, and 43) that contain the same peaks, the second is the most intense, but the first is still the most resolved. In both 93B spots 3 and 4, the base of these peaks slope downward to the right. The blue peaks in 93D

spot 1 slope upward to the right while spot 2 is flat across the summit. The variation is most likely due to the variation in the underlying $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) and has very little to do with the actual nature of the peaks in blue. Since the summit of the overall large peak is merely the sum of the $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) and the spectrum peaks (blue), it is possible that the peak fitting of the $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) resulted in the first few transition peaks being slightly off from their true center-of-gravity, FWHM, and area. Recall that the first four $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) present in all the spectra also have the greatest variability in center of gravity.

93B's spot 4 spectrum peaks (blue) are captured in Figure 45. Here, the spectrum range has been minimized from 3665 to 4050 Å isolating these peaks. The number of counts has been normalized to the largest peak. Next, a baseline from the $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) are subtracted providing just the spectrum peak spectrum.

Considering the collection methodology, it is difficult to know whether the spectrum is due to source or merely noise. Therefore, the overall curve is then smoothed using the adjacent-averaging method provided in *OriginPro*TM producing the red spectrum as shown. Twenty-one peaks are then fit off the smoothed curve with a R^2 value of 0.9974. Each of the four spectra containing spectrum peaks, along with all their peak centers of gravity, FWHMs, and areas are presented in Appendix C.

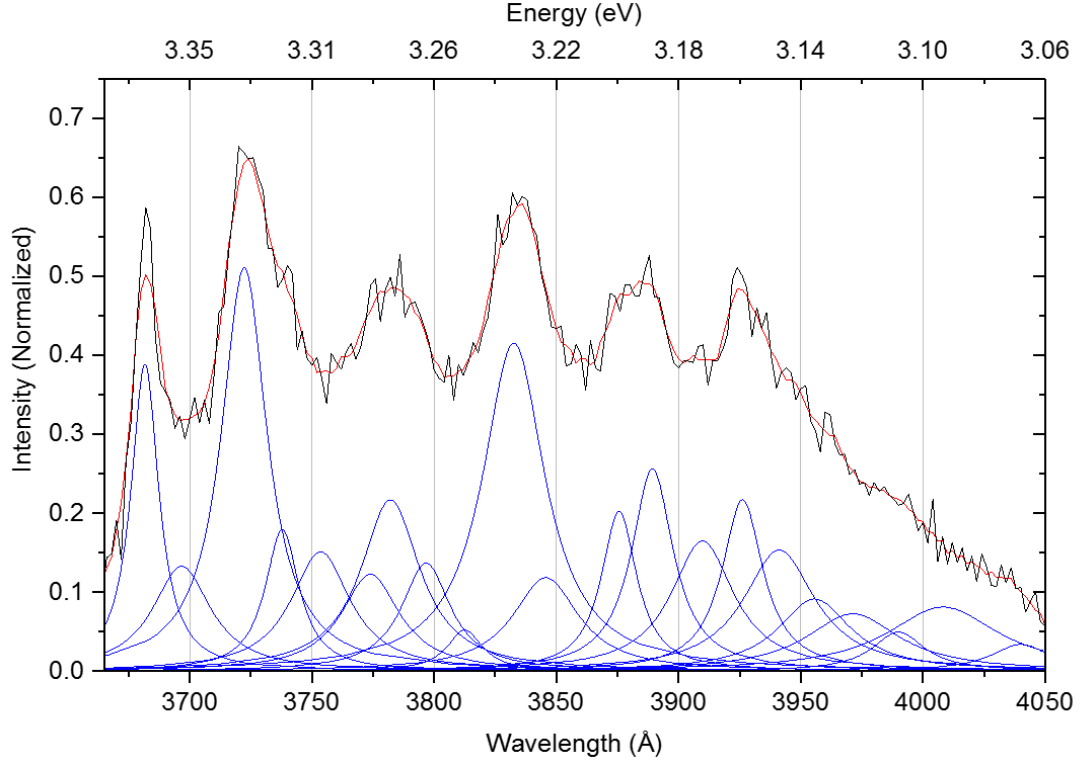


Figure 45. 93B PL spectrum of spot 3 (Blue peaks are were obtained by first normalizing, subtracting baseline, and smoothing).

If the assumption made earlier in this section that the $3639.3 \pm 21.0 \text{ Å}$ green peak represents the $5f^1 6d^1(e_g) (^2F_{5/2}) \rightarrow 5f^2 (^3H_4)$ transition, then the 3681.7 Å peak most likely represents a defect lying 39.2 meV below the conduction band as it is just below the conduction band at liquid helium temperature and highly resolved. This may be emission from some form of exciton annihilation. The subsequent broader peaks may be the result of additional free or donor/acceptor-bound exciton annihilations, shallow trap center recombination, DAP recombination, or one of the three phononically coupled. Each possibility is examined below.

There are no discernable smaller, highly resolved peaks at higher energy to the left of the 3681.7 Å peak, as Weisbuch and Bensity's work on GaAs showed, that could

be explained by (3) in Section 2.7.3 [77]. Their presence would be absolute proof that this peak is, in fact, an exciton. The fact that the crystal is highly defective all but rules out this defect being a free exciton. Here, the 39.2 meV is assumed to be the exciton binding energy. If true, this would be the first such value reported for single crystal UO₂. If one were to consider the possibility that the 3681.7 Å peak is the n=2 exciton peak of a possible n=1 exciton peak at 3722.3 Å, this would be erroneous. For the 3722.3 Å peak to have an n=2 exciton peak, that peak would fall at 3666.9 Å. If this logic is applied to all the other peaks as well, no other peak fits the n=2 exciton peak. Also, each subsequent peak FWHM increases compared to the first peak. Therefore, it is less likely that all the subsequent peaks are individual n=1 excitons and must be some other defect.

Since the subsequent peaks appear to occur in regular intervals, the next logical possibility is that the subsequent peaks are phonon replicas of the initial peak. However, when applying the physics of Section 2.7.2, the peaks were found not to occur in any of the published experimental LO and TO frequencies. To explore this, the 3681.7 Å peak was designated the ZPL. Utilizing Axe and Petitt's values for LO (556 cm⁻¹) and TO (285 cm⁻¹) frequencies, the multiple phonon peaks were calculated and then compared to the actual fitted peaks [42]. Only the 5x and 6x TO replicas of 3681.7 Å remotely matched the fitted peak. Performing the same analysis with the other reported values provides the same results, albeit with slightly dissimilar ω differences. Pang *et al.* provided a calculated LO frequency which was significantly different from their peers of 436.99 cm⁻¹ [44]. Yet, applying their value does not match our measurements.

However, when Yun *et al.*'s calculated LO value of 527.3 cm⁻¹ is used, the actual and the theoretical peaks are in good agreement as shown in Table 11. Five peaks are

shown as possible ZPL peaks with the first three having four phonon replicas, the fourth having three replicas, and the last having only two. Table 11 shows the resultant frequency from the peak fitting versus what the peaks should have been had each replica precisely observed the frequency. The actual and the theoretical data are then compared to show the percent difference. As can be seen, the difference between what is and what should have been are in good agreement. It is reasonable to assume that had the noise been reduced through better experimental procedure, the variability in the peak center-of-gravity could have been reduced, thus reducing the actual versus theoretical frequency differences even more.

Table 11. Designated ZPL peak with subsequent phonon replicas

Actual Values				Theoretical Values			Dif
Peak	Peak Center (Å)	Peak Center (cm ⁻¹)	ω (cm ⁻¹)	Peak Center (Å)	Peak Center (cm ⁻¹)	ω (cm ⁻¹)	ω (%)
ZPL	3681.7	27161.4	-	3681.7	27161.4	-	-
1x LO	3753.6	26641.1	520.3	3754.6	26634.1	527.3	1.3
2x LO	3832.6	26091.9	549.1	3830.4	26106.8	527.3	4.1
3x LO	3909.8	25576.8	515.2	3909.4	25579.5	527.3	2.3
4x LO	3989.9	25063.3	513.5	3991.7	25052.2	527.3	2.7
ZPL	3696.7	27051.2	-	3696.7	27051.2	-	-
1x LO	3773.9	26497.8	553.4	3770.2	26523.9	527.3	4.8
2x LO	3845.7	26003.1	494.7	3846.7	25996.6	527.3	6.4
3x LO	3926.2	25469.9	533.1	3926.3	25469.3	527.3	1.1
4x LO	4008.2	24948.9	521.1	4009.3	24942.0	527.3	1.2
ZPL	3722.3	26865.1	-	3722.3	26865.1	-	-
1x LO	3796.7	26338.7	526.4	3796.8	26337.8	527.3	0.2
2x LO	3875.7	25801.8	536.9	3874.4	25810.5	527.3	1.8
3x LO	3955.6	25280.6	521.2	3955.2	25283.2	527.3	1.2
4x LO	4040.0	24752.5	528.1	4039.4	24755.9	527.3	0.2
ZPL	3737.9	26753.0	-	3737.9	26753.0	-	-
1x LO	3812.5	26229.5	523.5	3813.1	26225.7	527.3	0.7
2x LO	3889.3	25711.6	517.9	3891.3	25698.4	527.3	1.8
3x LO	3971.3	25180.7	530.9	3972.8	25171.1	527.3	0.7
ZPL	3782.1	26440.3	-	3782.1	26440.3	-	-
1x LO	3860.9	25900.7	539.6	3859.1	25913.0	527.3	2.3
2x LO	3941.2	25373.0	527.7	3939.2	25385.7	527.3	0.1

Two peaks at 3681.7 and 3722.3 Å were chosen as the ZPL defects and their respective phonon replicas are shown in Figure 46. The other peaks are not shown in order to reduce the clutter in the figure. If it is true that many of the peaks in the spectrum are phonon replicas, this may be the first time the luminescence of such in single crystal UO₂ has been measured. However, it still does not help in the identification of the ZPL defects. It is important to address why the experimental research LO values did not match this experiment and why the theoretically calculated value did. Yun *et al.* states that their theoretical calculations are based on calculated lattice parameters slightly different from those used in the experiments. The theoretical lattice parameter value used is optimized

for the GCA/GCA+U approach used by Yun *et al.* in calculating the density of states (DOS) of electrons. Another possibility is that much of the past research into the material properties of UO_2 were conducted on thin films or poor quality crystals and by way of inelastic neutron scattering. Such material would be riddled with defects and have new defects introduced that could have significantly altered the vibrational states throughout the lattice. Lastly, of all the research cited in this report, none measured the precise stoichiometry of the samples both pre- and post-experiment. With UO_2 readily oxidizing, the $\sim 556 \text{ cm}^{-1}$ experimental LO value may have been for a UO_{2+x} stoichiometry, different from these samples.

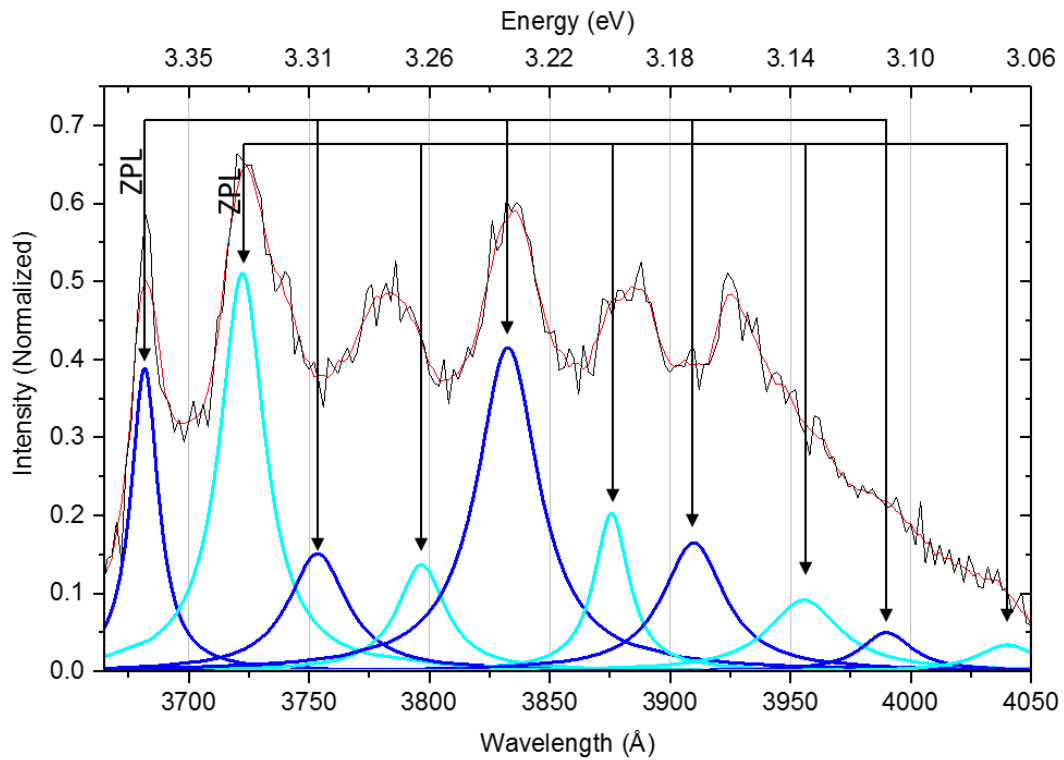


Figure 46. 93B PL spectrum of spot 3 with 2 ZPLs and subsequent phonon replicas.

The next potential investigated is that the ZPL peaks represent a series of extrinsic defects. There is a large body of research that has investigated and cataloged the luminescence of the transition and rare earth (RE) metals in solutions and compounds. The lanthanides, in particular, are well known for their brilliant luminescence that results from the same physics that governs U^{4+} luminescence, $d \leftrightarrow f$ and $f \leftrightarrow f$ transitions. From Ce to Tm, the various emission wavelengths and their associated transitions are well cataloged. When doped in fluorite, which has the same crystal structure as UO_2 , Er^{3+} (381 nm), Nd^{3+} (382 nm), Tb^{3+} (383 nm), Tm^{3+} (384 nm), and Pr^{3+} (399 nm) each emit luminescence that are candidates for our measured spectra [47]. None of the identified ZPLs agree with these values but a few of the replicas do. If the ZPL/replica designation is in fact incorrect, then the subsequent peaks may be the luminescence of these individual impurities.

Er^{3+} , Tb^{3+} , and Tm^{3+} also produce more intense, yet highly resolved luminescence at 454, 542, 543, 549, 552, and 561 nm. These peaks are not present in any of these spectra, providing further evidence that the spectral peaks (blue) are not the result of these RE impurities. Sm^{3+} and Eu^{3+} each produce a series of less intense peaks between 550 and 610 nm that could be the cause of the broad peak in this range in 93B's spot 4 spectrum. Recalling the XRF results in Section 4.2.1, a number of these elements were present in each spectra, albeit in very low atomic percentages. However, the literature has shown, based on the physics of $5d \rightarrow 4f$ transitions, only a small amount of these elements doped in solution or in a compound can produce brilliant luminescence. Therefore, without additional information, the conclusion cannot be made that these peaks are the resulting $5d \rightarrow 4f$ transitions of RE impurities, since erbium, terbium, praseodymium, and

neodymium were present in less than 50% of the XRF scans and mostly under 1% atomic percentage. Thulium was not present in any XRF data.

Another possibility is that the ZPL peaks are the result of defects, both intrinsic and extrinsic, serving as either donors or acceptors in the gap. The energy of these peaks indicate states near the band edge (NBE). Recall transitions 4, 5, 8, and 9 from Figure 5 in Section 2.7.3 depicting band-to-donor/acceptor and DAP recombination. Assigning specific elements to these defects is considerably more difficult as their energy levels are highly dependent upon a multitude of factors that are material dependent. Therefore, unlike the lanthanide $d \rightarrow f$ and $f \leftrightarrow f$ transition luminescence, there is no central repository for the catalog of all the possible donor/acceptor bound defects for every type of material in every possible material phase. Much of the relevant literature on comparable semiconductors that assigns certain elements to impurities from optical spectra do so by way of selectively doping the material and comparing the resulting spectra with the undoped spectra.

In discussing the presence of impurities, the photoluminescence of ZnO has shown a donor bound exciton (D^0X) at exactly 3.366 eV (3682 Å) [78]. The fact that four separate spectra of UO_2 have a peak at exactly this value may indicate one of two possibilities. First, in single crystal UO_2 , a D^0X or another defect species has exactly the same emission energy as a D^0X in ZnO. If this was the case, this also would be the first such value reported on single crystal UO_2 . The second option would be the presence of zinc in the crystal surface. This peak is also just below the reported band gap emission of single crystal ZnO at temperatures below 10 K [41][79][80]. The mineralizer used to

grow the UO_2 single crystals is known to contain trace amounts of zinc and could have been grown into the lattice. This, however, is not backed up by our XRF data.

The initial XRF scans from Section 4.2.1 showed no zinc in any of the samples except for spot 1 on 93E's beta side. Each scan spot on each sample was 100 μm in diameter with about 800 μm between each adjacent spot. Most of the surface was not scanned. Since the low percentage elemental makeup was considerably different at each spot, it is entirely possible that zinc could have been present in significant quantities at locations that were not scanned. Additionally, there was no way of ensuring that the PL beam fell in exactly the same spot as the XRF beam. Though the PL spectra could have been taken at a spot unscanned by XRF and contained high amounts of zinc, the absence of zinc in all but one of the 54 separate XRF spectra of the three samples makes a zinc transition an improbable explanation for the presence of the 3682 Å peak.

Though it is unlikely that zinc was initially present, a more likely explanation is that zinc was introduced to the surface during handling. In Section 3.7.4, it is mentioned that a ZnO crystal is used to calibrate the photoluminescence. The same forceps used to manipulate the ZnO crystal were also used to manipulate the UO_2 , albeit the samples were usually handled with forceps applied to the outside edges and not the faces. However, this was not strictly enforced. Perhaps a significant amount of ZnO had contaminated the UO_2 surface during handling, or a significant amount of zinc had contaminated the surface to bind with enough oxygen to form localized pockets of ZnO . In order to determine if zinc had been introduced, XRF scans were completed on these two sample faces after the PL measurements were obtained. Note that it is impossible to match the precise location of the scans on the sample when viewed from above as the

XRF camera views them. Additionally, the XRF camera does not focus at full magnification making it difficult to recognize features on the crystal face that can be used to navigate the scan marker. As a result, the scan locations were set as close to the original location as could be determined by aligning the sample in the optical microscope. These scans were made with the same settings as the original: 100 μm aperture at 30 keV for 10 minutes per scan.

Table 12 highlights the elemental breakdown of the updated scans. Only those elements above 1% are shown as in Table 6. Had zinc been introduced into the crystal, it would have been observed. Comparing the before and after XRF measurements shows the number of elements in 93B and D decreased by one. However, several are present in the pre- spectrum and not the post-, and vice versa; albeit in trace amounts. The fact that the uranium percentage is not exactly the same as in the initial measurements indicates that the XRF beam was not in the exact location in both measurements leading to scanning of different areas of the surface. However, it indicates that no major impurities have been introduced. Therefore, the 3681.7 Å peak is not the result of D^0X annihilation in ZnO . It could be D^0X annihilation, or another extrinsic defect, in UO_2 but there is no conclusive evidence of such.

Table 12. Overview of element makeup ($\geq 1\%$) of 93B's and 93D's α face.

93B (α)		K	Ge	As	Kr	Zr	Gd	Tb	Lu	W	Hg	Rn	Ra	U		
	Maximum	6.19	2.58	2.95	0.08	2.42	1.35	2.34	2.60	4.11	2.45	3.12	1.35	95.75		
	Minimum	2.08	0.12	0.12	0.08	2.20	1.34	0.15	0.94	0.14	0.34	0.32	0.58	86.66		
93D (α)		Al	Si	K	Ni	Ga	Se	I	Cs	Gd	Lu	Ta	Hg	At	Th	U
	Maximum	6.26	5.56	5.78	1.40	2.14	2.84	2.66	5.41	2.03	1.51	1.89	2.79	4.38	5.15	91.70
	Minimum	6.26	2.70	4.97	0.32	2.14	1.17	2.66	5.41	0.35	0.59	0.48	0.70	1.37	0.61	71.65

Without being able to establish the source of these five defects, the only way to characterize them is to identify their energy levels within the gap. It is unknown whether these are donor-related defects that are lying below the conduction band or acceptor-related lying above the valence band. It is also important to note that the $3708.8 \pm 1.9 \text{ \AA}$ peak in 93B's spots 1, 2, and 5 spectra is also most likely such a defect. This peak did not appear in any of the four spectra containing suspected NBE defect transition peaks (blue). Each of these six defects are shown in Figure 47 as NBE defects along with the $5f^1 6d^1 \rightarrow 5f^2$ known transitions. The five ZPL's are approximated using the drop down arrows to indicate the presence of their phonon replicas. As with the transition assignments, the NBE defect assignments are speculative in the absence of supplementary PL data or from complementary experimentation.

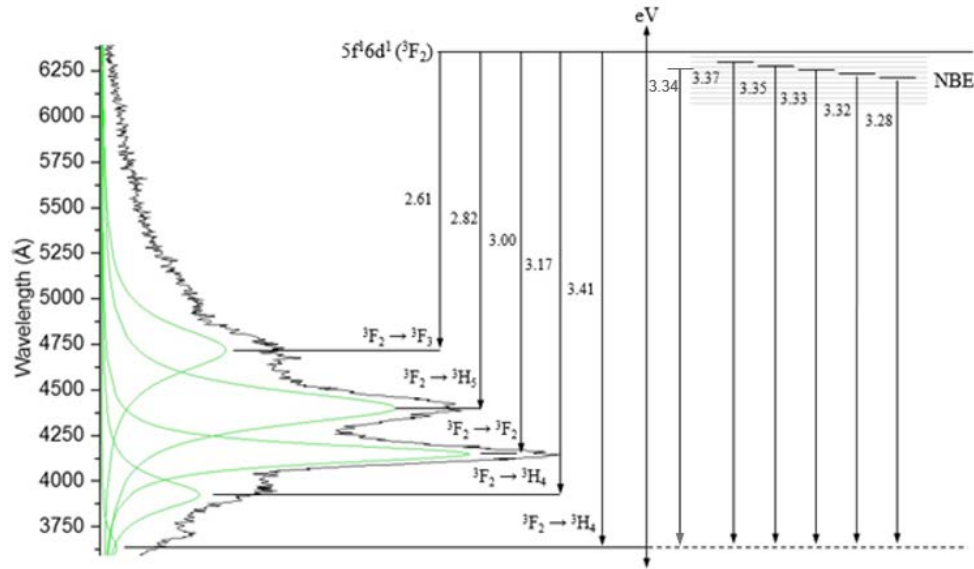


Figure 47. Assigned $5f^1 6d^1 ({}^3F_2) \rightarrow 5f^2$ transitions showing NBE defects depicted on 93B Spot 1 spectrum.

Molecular Vibrational Luminescence



Figure 48. 93B PL measurement spectra spot locations

Sample 93E was investigated much like 93D. Two locations were investigated with PL. These two locations produced the brightest luminescence. 93E was not as polished as 93B, nor as dull and rough as 93D. 93E's surface was scratched from the polishing process and had a large number of deep depressions on the surface as shown in Figure 48. Like 93D, 93E had briefly been previously exposed to the fluorospectrometer. It had also been previously loaded into the CL chamber along with 93D, but was never irradiated by electrons. The first spot investigated on the surface produced a greenish-blue color when illuminated by the PL laser. This was not present in 93B's spectra. The spectrum, shown in Figure 49, was taken at 0.8 seconds integration time, 1 Å step size, 1000 μm monochromator slit width, and at 9.4 K. Despite the fact that five spectra from 93B and two from 93D have already been discussed, this spectrum was chronologically the fourth taken of all the spectra immediately after 93B spot 3, and taken prior to having any knowledge of $5f^16d^1 \rightarrow 5f^2$ and uranyl emission. Anticipating sharp, well-resolved

peaks representative of a clearly defined band edge at $\sim 2\text{eV}$, the spectrum was taken from 4400 to 6400 Å.

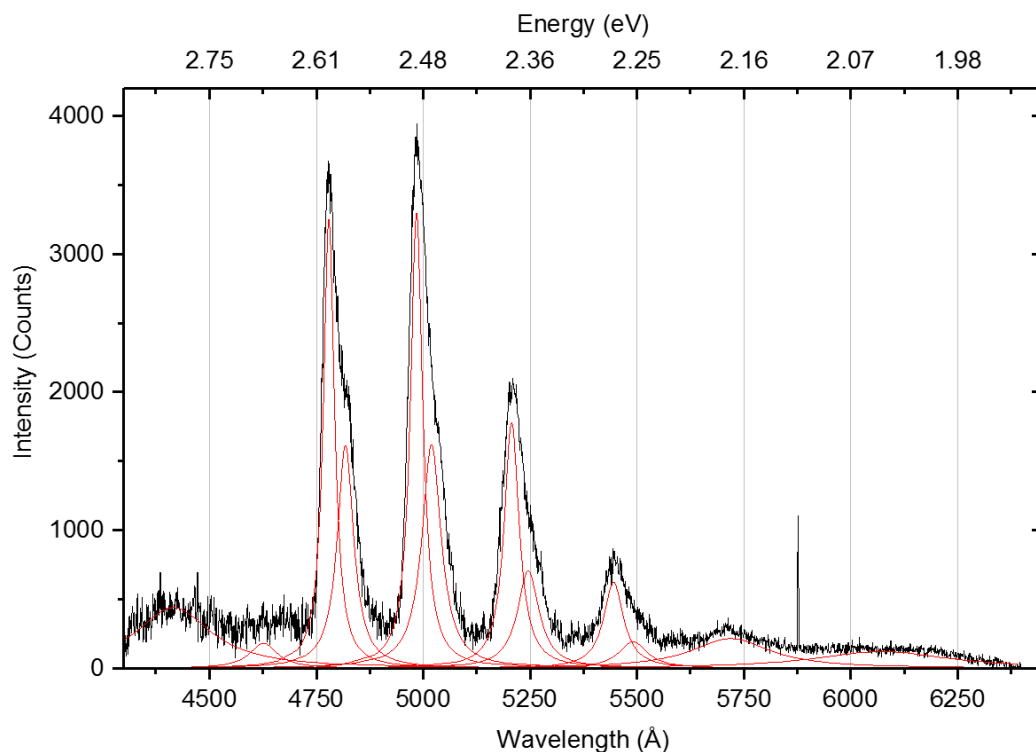


Figure 49. 93E PL spectrum of spot 1 (0.8s integration. time, 1 Å step size, 325nm excitation at 5mW, and at 9.4 K).

93E's spot 1 spectrum produced a series of five clearly defined peaks between 4750 and 5750 Å, characteristic of uranyl emission as discussed in Section 2.7.5. In addition, 5875 Å spectral line of helium is present. The spectrum was peak-fit in *OriginPro*TM with an R^2 value of 0.9780. The fitted peaks are shown in red in Figure 49. There are two smaller peaks to the left of the large peak at 4779.3 Å and one to the far right. Clearly, two peaks are evident in the composition of each of the four tallest peaks. These peaks occur at regular intervals of approximately 0.11 eV. The exact peak center-

of-gravity, full width at half maximum (FWHM), and peak area for each peak is detailed in Appendix D. Dieke and Duncan cataloged the fluorescence spectra of a large number of uranyl compounds [63]. Their work is used as a guide to characterizing these (suspected) uranyl emission spectra.

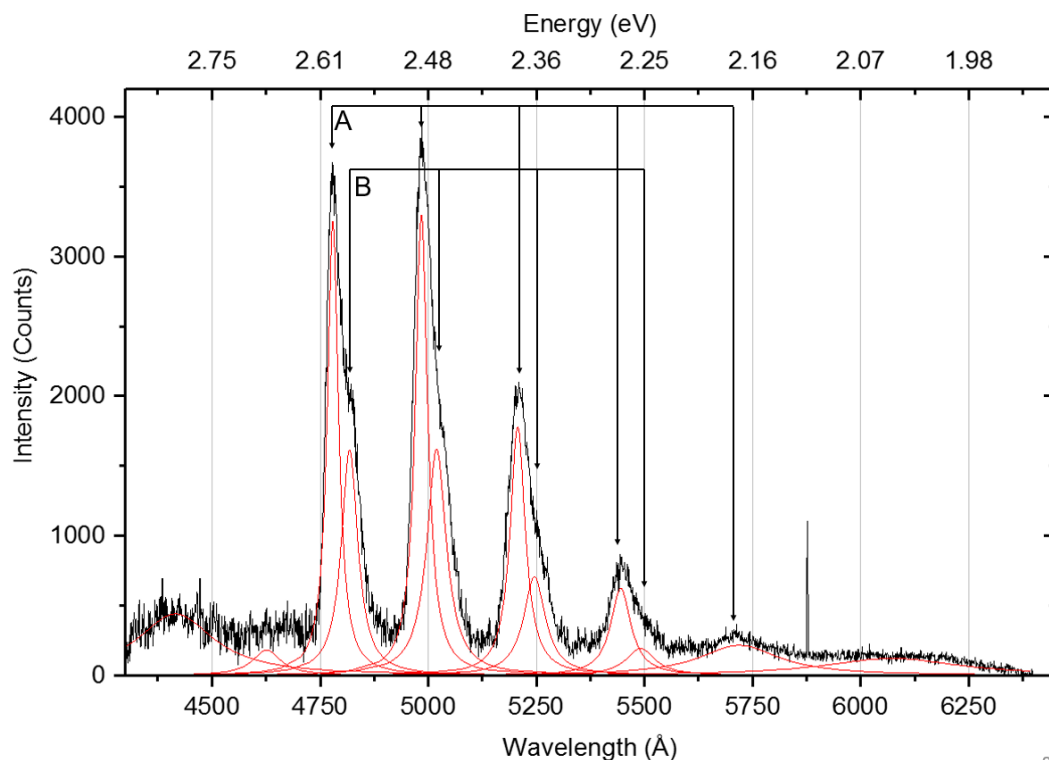


Figure 50. 93E PL spectrum at spot 1 with Uranyl series fitting

The bulk of uranyl emission literature have the first peak around 4800 Å, which is in good agreement with the 4779.3 Å peak. Utilizing (9) from section 2.7.5, the subsequent peaks can be divided into two distinct series of peaks as shown in Figure 50. Series A comprises the first fitted peak in each of the four doublets and the less intense broad peak at 5719.0 Å. Series B comprises the second fitted peaks in the each of the

doublets with no corresponding fifth peak. Both series can be described by modifying (9), as in (15).

$$v_{fluorescence} = v_f - n_s v_s - \cancel{n_s v_s} - \cancel{n_s v_s} = \sum n_i v_i \quad (15)$$

In (15) there is no contribution from the antisymmetric and bending vibrations. The first peak in series A is merely the pure electronic transmission, v_f , and the four subsequent series A peaks represent the symmetric vibrational contribution at sequential quantum numbers, n . Series B can be explained similarly, except that the offset from series A is attributed to defect-related vibrations inherent in the crystal. These results are shown in Table 13. The intensity of each fitted peak is labeled either strong (str.), medium (m.), weak (w.), or very weak (v.w.) as is common in the literature. The resultant values for Δv_s ($854.4 \pm 14.1 \text{ cm}^{-1}$) and Δv_i ($150.7 \pm 11.2 \text{ cm}^{-1}$) are in good agreement with literature [63]. However, it is important to note that no uranyl emission data has ever been presented that has come from the oxidation of single crystal UO_2 . Though these values fall within the ranges presented in literature, if it is truly uranyl emission, this is the first time these values have been documented.

Table 13. Uranyl series A & B in the PL spectrum of 93E at spot 1

Series	Peak	$v_{fluorescence}$	Intensity	λ (Å)	v (cm^{-1})	Δv_s (cm^{-1})	Δv_i (cm^{-1})
A	3	$v_f - (0)v_s$	str.	4779.3	20923.6	-	-
	5	$v_f - (1)v_s$	str.	4984.4	20062.6	861	-
	7	$v_f - (2)v_s$	m.	5206.7	19206.0	856.6	-
	9	$v_f - (3)v_s$	m.	5445.1	18365.1	840.9	-
	11	$v_f - (4)v_s$	w.	5719.0	17485.6	879.5	-
B	4	$v_f - (0)v_s - v_i$	m.	4818.1	20755.1	-	168.4
	6	$v_f - (1)v_s - v_i$	m.	5019.4	19922.7	832.4	140.0
	8	$v_f - (2)v_s - v_i$	w.	5245.6	19063.6	859.1	142.3
	10	$v_f - (3)v_s - v_i$	v.w.	5490.6	18212.9	850.7	152.3

93E's spot 2 spectrum produced what seems to be a mixture of all of 93Bs spectra and 93E's spot 1. When the PL laser beam was placed on this spot, the luminescence returned to a more blue color. Anticipating a spectrum more reminiscent of those in section 4.2.3, the range was increased back to 3500 to 6400 Å. The spectrum, shown in Figure 51, was taken at 0.4 seconds integration time, 5 Å step size, 1000 μm monochromator slit width, and at 10 K.

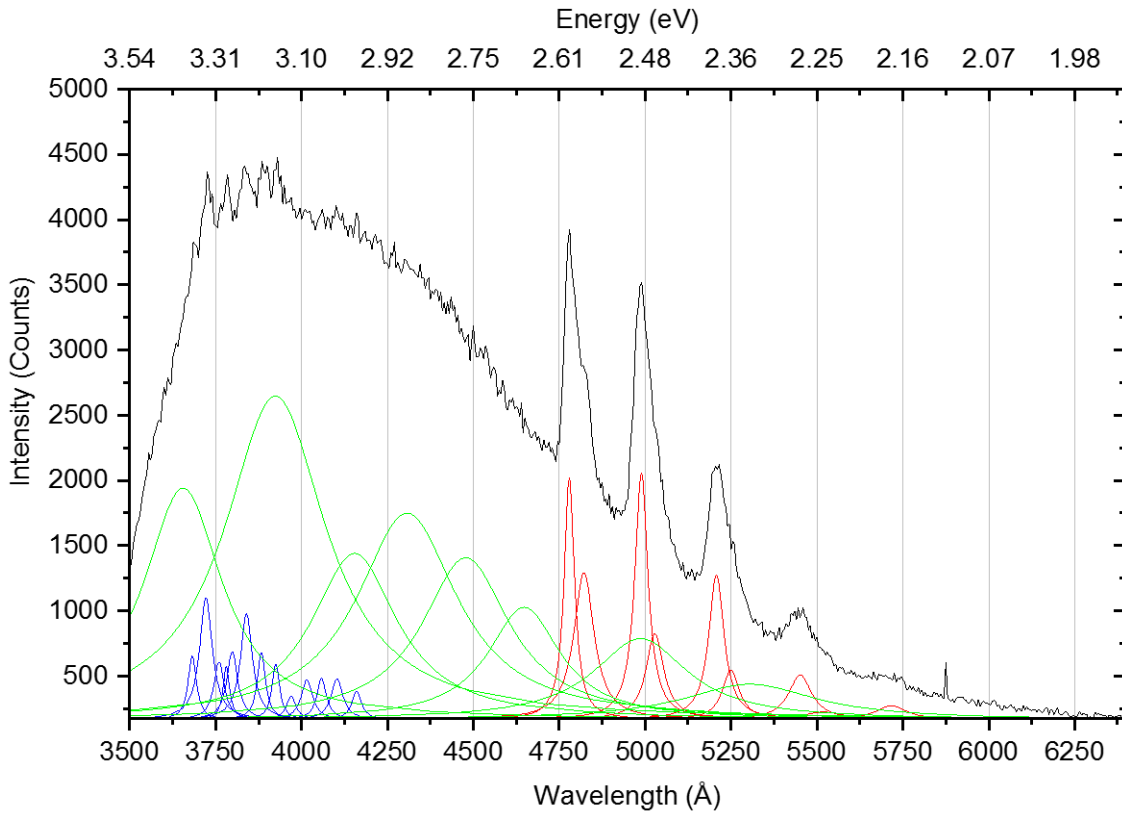


Figure 51. 93E PL spectrum at spot 2 (0.4s integration. time, 5 Å step size, 325nm excitation at 5mW, and at 10K)

The Spectrum is then peak fit with green peaks representing $5f^{16}d^1 \rightarrow 5f^2$ emission, red peaks for uranyl emission, and blue peaks for suspected NBE defect and phonon emission. The R^2 value is 0.9983. With this spectrum being considerably more complex than previous spectra, the red peaks were fit first using 93E's spot 1 as a guide. Next, the

suspected NBE defect transition peaks (blue) were fit using the data from the previous section as a guide. Lastly, the $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) were fit and allowed to fill in the remainder of the spectrum. As a result, both the NBE defect transition peaks (blue) and $5f^16d^1 \rightarrow 5f^2$ transition peaks (green) are in excellent agreement with the previous spectra.

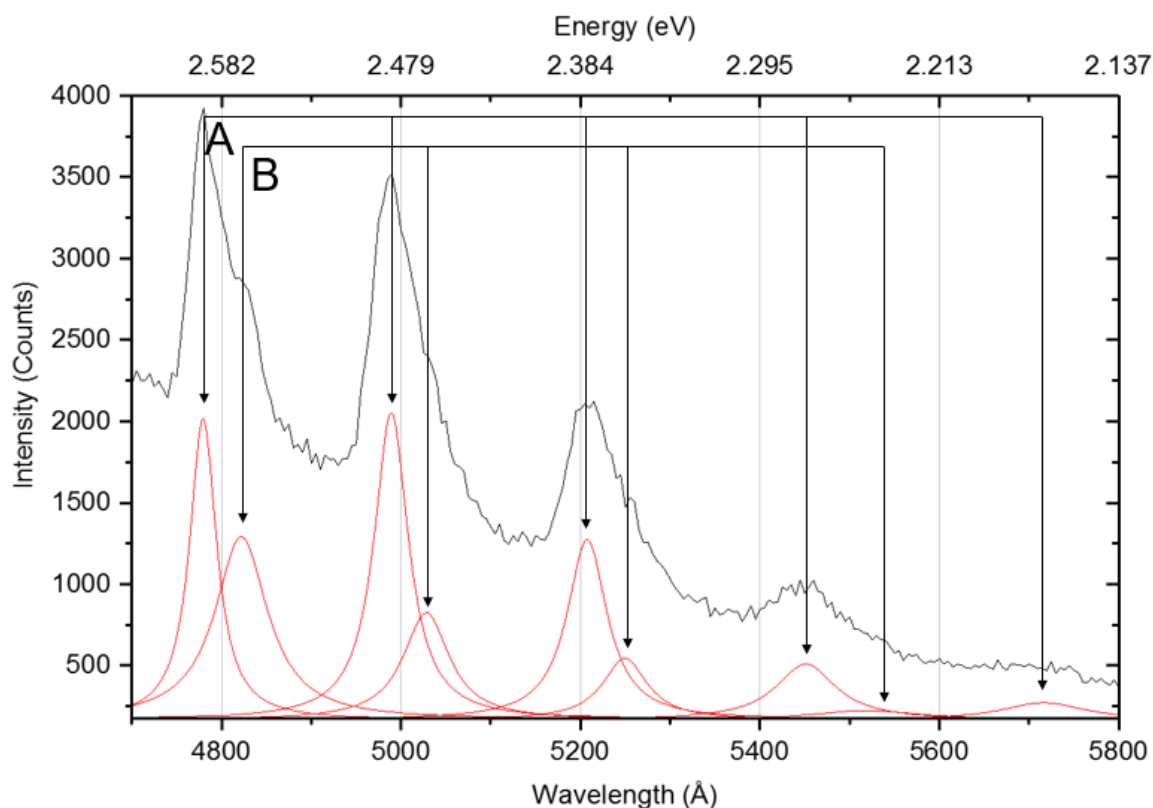


Figure 52. 93E PL spectrum of spot 2 showing uranyl series spectrum

Figure 52 shows the spectrum magnified around the peaks (red). These peaks are characterized the same way as were those from spot 1. Series A represents the pure electronic transition coupled with its sequential symmetric vibrations. Series B represents series A offset by the defect-related vibrations inherent within the crystal. The resultant values for $\Delta\nu_s$ ($858.9 \pm 17.1 \text{ cm}^{-1}$) and $\Delta\nu_i$ ($169.3 \pm 16.4 \text{ cm}^{-1}$) are in good

agreement with literature [63]. The Δv_s value is in excellent agreement with 93E spot 1, while the Δv_i value has increased by 12.3%. The results are shown in Table 14. Spot 2 is interesting in that both types of emission in this research are present. Unlike any other spot on these three samples, this spot had enough of both oxidation states within the $\sim 80\mu\text{m}$ radius laser beam cross-section for each type to stand out.

Table 14. Uranyl series A & B in the PL spectrum of 93E spot 2

Series	Peak	$\nu_{\text{fluorescence}}$	Intensity	λ (Å)	ν (cm ⁻¹)	Δv_s (cm ⁻¹)	Δv_i (cm ⁻¹)
A	1	$\nu_f - (0)\nu_s$	str.	4779.3	20923.6	-	-
	3	$\nu_f - (1)\nu_s$	str.	4989.0	20044.1	879.5	-
	5	$\nu_f - (2)\nu_s$	str.	5207.4	19203.4	841.1	-
	7	$\nu_f - (3)\nu_s$	m.	5451.2	18344.6	851.9	-
	9	$\nu_f - (4)\nu_s$	w.	5716.2	17494.1	865.9	-
B	4	$\nu_f - (0)\nu_s - \nu_i$	m.	4821.9	20738.7	-	185.1
	6	$\nu_f - (1)\nu_s - \nu_i$	m.	5028.2	19887.8	848.2	153.5
	8	$\nu_f - (2)\nu_s - \nu_i$	w.	5249.5	19049.4	840.1	152.5
	10	$\nu_f - (3)\nu_s - \nu_i$	v.w.	5519.4	18117.9	885.7	186.3

93D was the only other sample to produce a spectrum characteristic of uranyl emission. Shown as spot 3 in Figure 41, this location produced bright green emission when exposed to the laser beam. Anticipating a spectrum more reminiscent of spot 1 with no U^{4+} emission present, the range was changed to 4400 to 6400 Å. The spectrum, shown

in Figure 53, was taken at 1.2 seconds integration time, 0.5 Å step size to increase the amount of detail. It is further magnified to highlight the peaks.

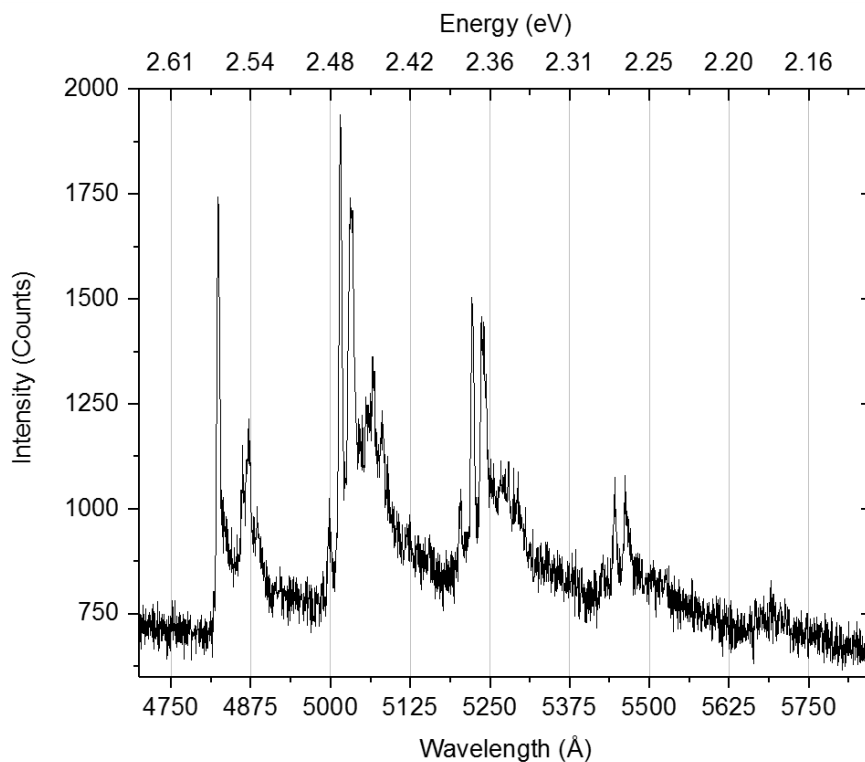


Figure 53. 93D PL spectrum of spot 3 (1.2s integration time, 0.5 Å step size, 325nm excitation. at 5mW, and at 10 K)

In this measurement, there are five sets of peaks, as with the previous spectra. However, unlike any of the spectra measured thus far, each of the five peaks can be further resolved into a cluster of peaks. Not only are the clusters at regular intervals of 0.98x eV, the individual peaks within the clusters, when paired with their respective peer peak in the next cluster, also occur at the same interval. There is much precedence in Dieke and Duncan's work for the fine resolution of multiple peaks per cluster at low

temperature: unfortunately, not for any single crystal uranium compound. Turning again to (9), the peaks are fit in a similar manner as previously, albeit with greater difficulty.

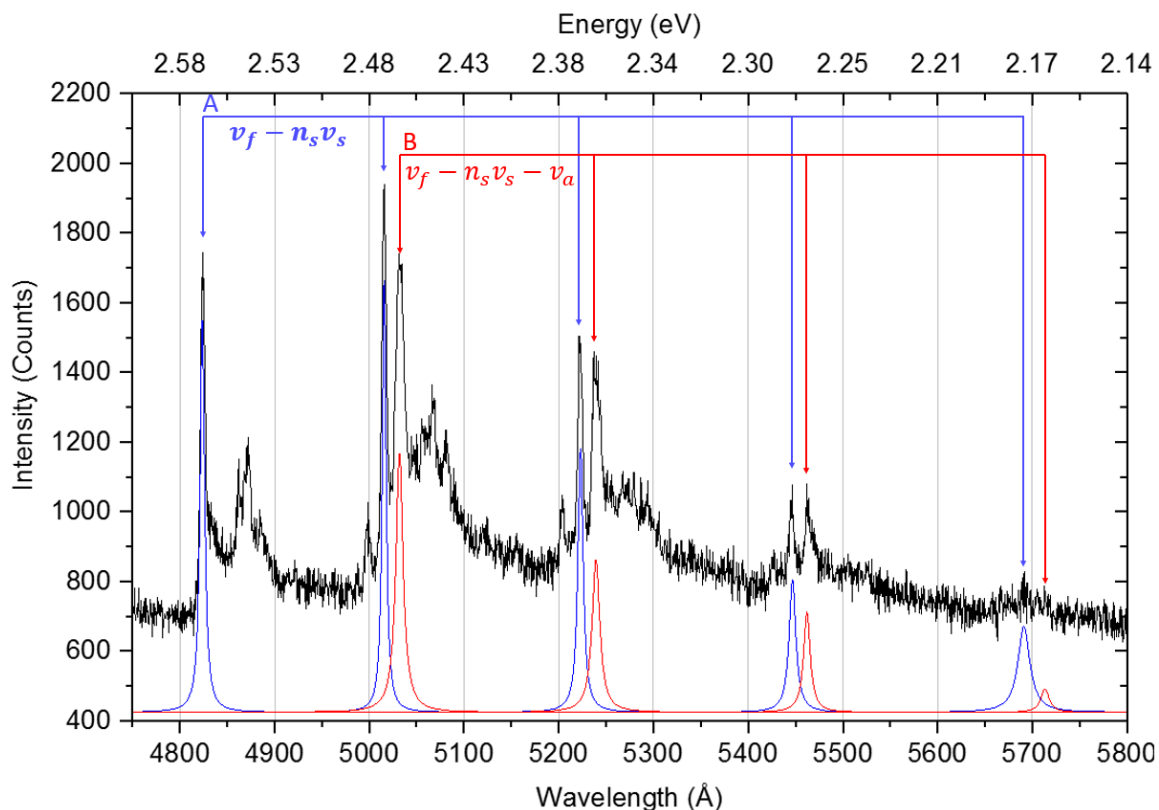


Figure 54. 93D PL spectrum at spot 1 with Uranyl series A and B fitting

Working methodically, from simplicity toward complexity, those peaks that result solely from the symmetric vibrations are fit first, starting with the first overall peak labeled A. Next, the same series but offset by the antisymmetric vibrational frequency is labeled B and shown in Figure 54. Series A has a Δv_s of $790.0 \pm 2.7 \text{ cm}^{-1}$. This is about an 8% decrease from the previous spectra. The fact that there is low local variability of the A peaks is a good indication that these peaks are in fact the correct series relation. Series B has a Δv_s value of $790.3 \pm 11.1 \text{ cm}^{-1}$, and is offset from series A by 850.8 ± 7.7

cm^{-1} , the Δv_a value. Shown in Table 15, the Δv_s value is consistent with series A and the Δv_a is consistent with literature.

Table 15. Uranyl Series A & B in the PL spectrum of 93D

$v_{\text{fluorescence}} = v_f - n_s v_s - n_a v_a - \sum n_b v_b - \sum n_t v_t$								
Series A	λ (Å)	ν (cm^{-1})	Δv_s (cm^{-1})	Series B	λ (Å)	ν (cm^{-1})	Δv_s (cm^{-1})	Δv_a (cm^{-1})
$\nu_f - (0)\nu_s$	4823.7	20730.9	-	$\nu_f - (0)\nu_s - \nu_a$	5031.9	19873.3	-	857.6
$\nu_f - (1)\nu_s$	5015.7	19937.3	793.6	$\nu_f - (1)\nu_s - \nu_a$	5239.3	19086.5	786.8	850.8
$\nu_f - (2)\nu_s$	5223.0	19146.1	791.3	$\nu_f - (2)\nu_s - \nu_a$	5462.1	18307.8	778.7	838.3
$\nu_f - (3)\nu_s$	5446.9	18359.2	786.9	$\nu_f - (3)\nu_s - \nu_a$	5713.4	17502.6	805.3	856.6
$\nu_f - (4)\nu_s$	5691.2	17571.1	788.0	$\nu_f - (4)\nu_s - \nu_a$	-	-	-	-

Next, expanding (9), the bending vibration is considered. There is precedence in Dieke and Duncan's work for multiple bending vibrations. Shown as Series A offset by the three bending vibrational frequencies in Figure 55, these peaks are only present in the first three clusters of the spectrum. The three frequencies are $171.4 \pm 4.4 \text{ cm}^{-1}$, $205.3 \pm 0.9 \text{ cm}^{-1}$, and $254.6 \pm 1.9 \text{ cm}^{-1}$. In addition, the resultant Δv_s values are consistent. The bending frequencies are shown in detail in Table 16. The remainder of the fitted peaks, all possible combinations of the five terms in (9), are shown in Appendix D along with the fully fitted spectrum.

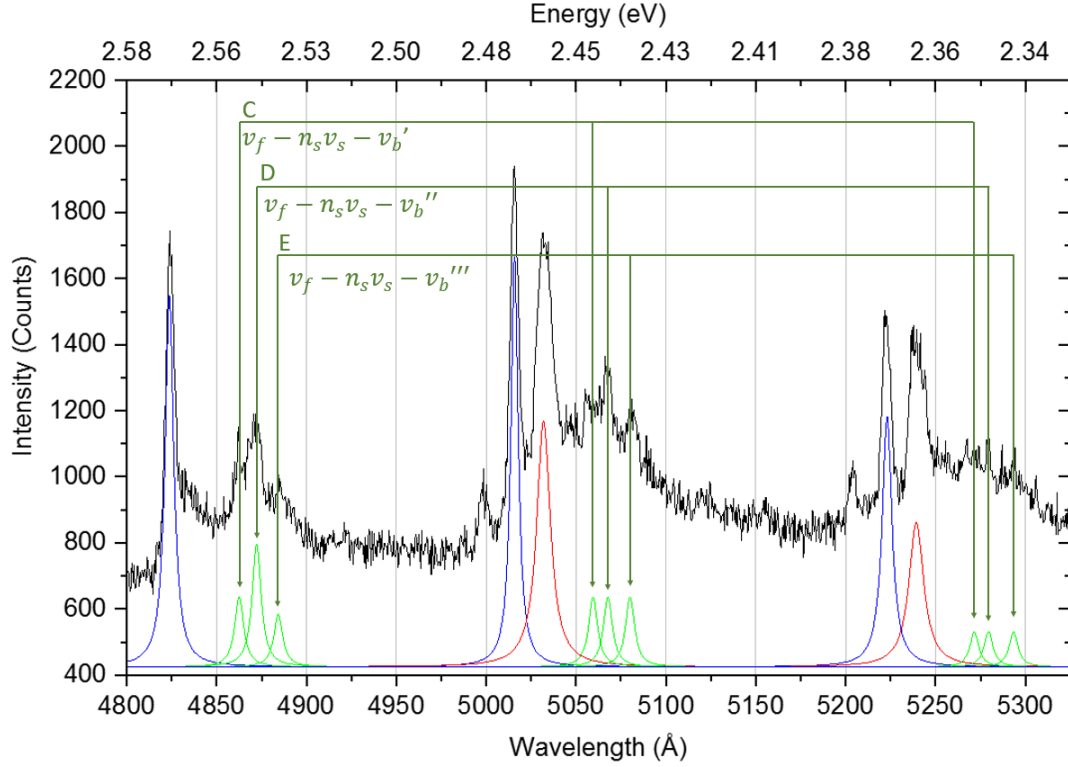


Figure 55. 93D PL spectrum of spot 1 Uranyl series C, D, and E fitting using bending vibrational modes.

Table 16. Uranyl series C, D & E in the PL spectrum of 93D

$v_{fluorescence} = v_f - n_s v_s - n_b v_b = \sum n_i v_i$				
Series C	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_b$ (cm ⁻¹)
$v_f - (0)v_s - v_{b'}$	4862.6	20565.3	-	165.6
$v_f - (1)v_s - v_{b'}$	5059.4	19765.1	800.3	172.3
$v_f - (2)v_s - v_{b'}$	5271.5	18969.8	795.2	176.0
$v_f - (3)v_s - v_{b'}$	-	-	-	-
$v_f - (4)v_s - v_{b'}$	-	-	-	-
Series D	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_{b''}$ (cm ⁻¹)
$v_f - (0)v_s - v_{b''}$	4872.3	20524.4	-	206.5
$v_f - (1)v_s - v_{b''}$	5067.7	19732.7	791.7	204.6
$v_f - (2)v_s - v_{b''}$	5279.4	18941.4	791.3	204.7
$v_f - (3)v_s - v_{b''}$	-	-	-	-
$v_f - (4)v_s - v_{b''}$	-	-	-	-
Series E	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_{b'''}$ (cm ⁻¹)
$v_f - (0)v_s - v_{b'''}$	4884.3	20473.9	-	257.1
$v_f - (1)v_s - v_{b'''}$	5080.0	19685.0	788.9	252.3
$v_f - (2)v_s - v_{b'''}$	5293.3	18891.7	793.3	254.4
$v_f - (3)v_s - v_{b'''}$	-	-	-	-
$v_f - (4)v_s - v_{b'''}$	-	-	-	-

Each of the Δv_b frequencies are in agreement with the ranges provided in literature [63]. The Δv_s , Δv_a , and Δv_i frequencies of 93D's spot 3 spectrum are 797.6 ± 6.1 , 850.8 ± 7.7 , and $50.9 \pm 6.6 \text{ cm}^{-1}$ respectively. However, there are no reported values for the uranyl emission stemming from single crystal UO_2 oxidation. Therefore, the fact that Δv_s is towards the bottom of the reported range in literature does not indicate these values are in error. In fact, since Dieke and Duncan's work was conducted immediately after the Manhattan Project with the technology available at the time, many of the reported values may require adjustments if they were to be re-measured with precise modern instrumentation. The reduction in Δv_i from 93E spots 1 and 2 is a result of a reduction in the local defect population. This spot on 93D lacks the damage (i.e., scratches and impurities) that are present in the two other spots. This is further evident by the fact that the spectrum is dominated by many narrow FWHM peaks. However, the fact that uranyl emission is so prevalent indicates a significant amount of oxidation that would produce a large number of intrinsic defects.

In the previous section, all of the spectra had fitted peaks in the wavelength range consistent with these uranyl peaks. In fact, $5f^16d^1 \rightarrow 5f^2$ transition assignments were withheld until the possibility of uranyl emission could be ruled out. In Table 17, each of the fitted peaks whose wavelength merited nomination of that peak as a uranyl emission candidate is shown with the frequency between peaks. As evident by the large variability in frequency between peaks within each spectrum and between spectra, these peaks, as fitted, are not credible candidates for uranyl emission. However, this does not prove these are the result of $5f^16d^1 \rightarrow 5f^2$ transitions either. Had the spectra been taken with more detail, perhaps the peak fitting would have produced more consistent and clearer results.

Table 17. Uranyl candidates from Section 4.2.3

Peak	93B Spot 1			93B Spot 2			93B Spot 3		
	Peak	Peak	ω	Peak	Peak	ω	Peak	Peak	ω
	(Å)	(cm-1)	(cm-1)	(Å)	(cm-1)	(cm-1)	(Å)	(cm-1)	(cm-1)
1	4719.0	21190.9	-	4772.4	20953.8	-	4744.6	21076.6	-
2	5026.1	19896.1	1294.8	4984.9	20060.6	893.2	5012.9	19948.5	1128.1
3	5218.4	19163.0	733.1	5198.9	19234.8	825.8	5203.6	19217.5	731.0
4	5456.3	18327.4	835.6	5423.8	18437.3	797.5	5456.6	18326.4	891.1
5	5646.6	17709.8	617.6	5617.3	17802.1	635.2	5639.4	17732.4	594.0
6	-	-	-	-	-	-	-	-	-
Peak	93B Spot 4			93B Spot 5			93D Spot 1		
	Peak	Peak	ω	Peak	Peak	ω	Peak	Peak	ω
	(Å)	(cm-1)	(cm-1)	(Å)	(cm-1)	(cm-1)	(Å)	(cm-1)	(cm-1)
1	4733.1	21127.8	-	4733.1	21127.8	-	4749.2	21056.2	-
2	5025.8	19897.3	1230.5	5025.8	19897.3	1230.5	5020.8	19917.1	1139.1
3	5202.7	19220.8	676.5	5202.7	19220.8	676.5	5234.1	19105.5	811.6
4	5468.3	18287.2	933.6	5468.3	18287.2	933.6	5471.9	18275.2	830.3
5	5631.6	17756.9	530.3	5631.6	17756.9	530.3	-	-	-
6	5755.3	17375.3	381.6	5755.3	17375.3	381.6	5796.3	5796.3	12478.9
Peak	93D Spot 2								
	Peak	Peak	ω						
	(Å)	(cm-1)	(cm-1)						
1	4733.4	21126.6	-						
2	5010.1	19959.7	1166.9						
3	5234.1	19105.5	854.2						
4	-	-	-						
5	5632.6	17753.8	1351.7						
6	-	-	-						

4.3 Summary

A body of literature concerning the electronic structure and optical properties of UO_2 has been methodically laid out. Uranium's 5f orbital contributes to unusual bonding and electronic structural properties unique to the actinides and lanthanides that greatly differentiates its optical properties from those of more established semiconductors. Only once a thorough understanding of the electronic structure was understood could the optical spectrum be accurately analyzed.

Seven spectra from two samples produced consistent results for the emission of U^{4+} in UO_2 . Specific $5f^16d^1 \rightarrow 5f^2$ transitions were tentatively assigned to the first five peaks, as these were present in each spectrum, were the most intense, and the most resolved. These values are consistent with the literature for U^{4+} emission. No such values for single crystal UO_2 exist in literature. Additionally, five defects were shown below the band edge, each with assigned phonon replicas. The defects could not be identified given the data. These assignments are shown in Table 18.

Table 18. $5f^16d^1 \rightarrow 5f^2$ transition assignments and NBE defect locations

Emission Wavelength (Å)	Energy (eV)	$5f^16d^1 \rightarrow 5f^2$ Transition	NBE Defect Wavelength (Å)	NBE Defect Energy (eV)
3639.3 ± 21.0	3.41 ± 0.02	$^3F_2 \rightarrow ^3H_4$	3681.7	3.37
3914.0 ± 26.7	3.17 ± 0.02	$^3F_2 \rightarrow ^3H_4$	3722.3	3.33
4138.3 ± 21.4	3.00 ± 0.02	$^3F_2 \rightarrow ^3F_2$	3737.9	3.32
4398.2 ± 23.5	2.82 ± 0.02	$^3F_2 \rightarrow ^3H_5$	3773.9	3.28
4740.5 ± 15.8	2.61 ± 0.01	$^3F_2 \rightarrow ^3F_3$	3782.1	3.28

Three sites on two samples produced uranyl emission because of oxidation at that location. Each spectrum was fit to identify the frequencies associated with the vibration mechanism outlined in Section 2.7.5. These frequencies are averaged and collectively presented in Table 19. There are no values for any of these vibrational frequencies for uranyl emission in single crystal UO_2 anywhere in literature. Each value is consistent with the range for uranyl emission in uranium compounds

presented in literature. Peaks in 93D spot 3 were considerably more resolved and resulted in a lower Δv_s and higher Δv_i frequency than the previous two spots.

Table 19. All uranyl series averages

	93E Spot 1		93E Spot 2		93D Spot 3	
	Average	STDEV	Average	STDEV	Average	STDEV
Δv_s (cm ⁻¹)	854.4	14.1	858.9	17.1	797.6	6.1
Δv_a (cm ⁻¹)	-	-	-	-	850.8	7.7
$\Delta v_{b'}$ (cm ⁻¹)	-	-	-	-	171.4	4.4
$\Delta v_{b''}$ (cm ⁻¹)	-	-	-	-	205.3	0.9
$\Delta v_{b'''}$ (cm ⁻¹)	-	-	-	-	254.6	1.9
Δv_i (cm ⁻¹)	150.7	11.2	169.3	16.4	50.9	6.6

V. Conclusions and Recommendations

5.1 Conclusions

PL was conducted on three similar samples of single crystal UO_2 using a 5mW HeCd laser (325nm) at approximately 10 K in a 10^{-6} Torr vacuum. It is believed that elements of the electronic structure of single crystal UO_2 has been measured for the first time using PL. $13\ 5f16d1 \rightarrow 5f^2$ transitions, depicted in LS notation, are assigned to the measurement wavelengths. Additionally, NBE defects, most likely extrinsic, have been cataloged but not identified. Additional defect characterization is needed to identify each NBE defect. Each defect is accompanied with multiple LO phonon replicas. The LO phonon frequencies measured agree with those published by Yun *et al* [45].

It can also be definitively concluded that single crystal UO_2 , as suggested by the literature and predicted by the physics, is unstable at the surface and readily oxidizes to such a the degree that uranyl compounds form in densities sufficient enough to be measured by PL. It is believed that the uranyl emission spectra are the first such measurements taken of uranyl emission stemming from the surface oxidation of single crystal UO_2 . The degree of oxidation at the precise location measured by the PL laser was unable to be determined with the equipment available. The areas measured that had visible damage, e.g., surface discoloration on spots 3 and 4 on 93B, did not present uranyl emission. Those areas that did produce uranyl emission visually appeared homogenous and smooth. In addition, whether the oxidation experienced was the result of prolonged

exposure to air or accelerated processes due to handling and/or other experimentation is also yet to be determined.

From the XRF and gamma spectroscopy results, no significant impurity, other than remnants of the thorium seed crystal, exists homogenously throughout the entire crystal surface following growth. One face of all three samples was considerably more homogenous than the other face. The face with a greater population of impurities, both in number of elemental species and atomic percentage, was labeled the β face and withheld from measurements. Each sample face contained isolated pockets of impurities in quantities above 5% atomic composition. The impurities are believed to come from the feedstock and/or the mineralizer used during growth, but no further investigation was conducted. Post-PL XRF measurements were conducted on 93B and 93D to determine whether additional impurities were added during experimentation through handling, but the results are inconclusive.

Engineering a detection device made from these samples as-is would be difficult. With large variability in the oxidation levels and surface defects across the surfaces, taking electronic measurements such as Hall measurements would vary depending upon the probe locations. Any sample incorporated into a device would have to be polished to ensure a near uniform surface stoichiometry and fabricated, maintained, and stored in a clean and preferably oxygen-free/deprived environment. Passivation of exposed surfaces would be necessary to reduce changes to electronic structure due to oxidation.

5.2 Recommendations

Improvements for this research can be broken down into two categories: methodology and equipment. First, as had been discussed at multiple points in the analysis section, the data acquisition methodology was inconsistent. Had a thorough understanding of the electronic structure been understood at the start of the experimentation, the methodology would have been more uniform and the areas that needed further investigation given their proper attention. Further hindering this was that all the PL data had to be taken by a technician as the equipment did not belong to AFIT nor was this researcher allowed to operate it. This greatly hindered the methodology, as data had to be quickly collected while the technician was available. The researcher was not afforded the time to ponder the results and experiment with the equipment.

Secondly, much of the original experiment was abandoned due to equipment problems. AFIT's fluorospectrometer was unable to take data in vacuum and at any cryogenic temperature, thus necessitating collaboration with AFRL for PL measurements. Fortunately, the AFRL PL system was a state-of-the-art system that provided good data despite bad methodology. AFIT's CL system broke without a replacement available in time for data collection. The best way to safeguard against the issues that prevented the CL measurements is to have the machine up and routinely running in the months leading up to the research actually being conducted. This would provide ample response time to correct issues.

If it is desired to improve upon this work, the following recommendations are made. First, it is essential that any PL data be taken with a low wavelength, quality laser (e.g., *Kimmon Koha Co., LTD.* IK series helium-cadmium (HeCd) 325 nm laser), with the

highest resolution monochromator available, in a strong vacuum, and at the lowest cryogenic temperature possible. Without all these ingredients, the fidelity needed to discern such a defective crystal would be absent.

Any equipment improvements over what was used in this experiment, if available, is essential. If access is available to a microscopic PL system that can also take Raman measurements at that same location on the sample, this avenue should be pursued. This would not only allow for PL measurements to be conducted, but also for pre- and post-PL Raman measurements to be conducted at that same location. This would identify the oxidation level pre- and post-PL and confirm experimentally induced-oxidation. The system would have to be able to achieve liquid-helium temperatures and vacuum as discussed above to be of benefit. Any PL spectra needs to be obtained at a low power setting initially and then dialed up slowly until the resulting spectrum is to the researcher's liking. This will prevent damage to the surface by laser energy deposition. For every spectral measurement, no matter what wavelength range, multiple measurements should be taken to allow the averaging of the spectrum. In addition, utilizing a cryogenically cooled PMT would greatly reduce noise. DFT calculations would significantly help to verify the results discussed. Since DFT calculations are very specific and time consuming, collaborating this experimental approach with a computational one early in the academic year would be wise.

Appendix A

MCNP6 Source Code

UO2 Sim

C ***** Block 1: Cells

1	1	-10.97	-1001	imp:N=1	\$UO2 Sample
2	2	-1.225e-3	-1000 1001	imp:N=1	\$Air surrounding sample
3	0		1000	imp:N=0	\$Outside sphere

C ***** Block 2: Surfaces

1000	SO	20		\$ sphere surround everything
1001	RPP	0.28 .964 -0.233 0.233 -0.509 0.509		\$.686cm x .465cm x .118 mm

C ***** Block 3: Data

Mode n

Nps 1e6

C *****material

m1	92238	0.323072		\$ UO2
	8016	0.666667		
m2	6000	-0.000124		\$ Air
	7014	-0.755268		
	8016	-0.231781		
	18000	-0.012827		

C *****source

sdef erg 2.5 pos 0 0 0 vec 1 0 0 dir d1
si1 -1 0.995 1
sp1 0 0.95 0.05
sb1 0 0 1
cut:N J 2.5e-8
f7:N 1

Appendix B

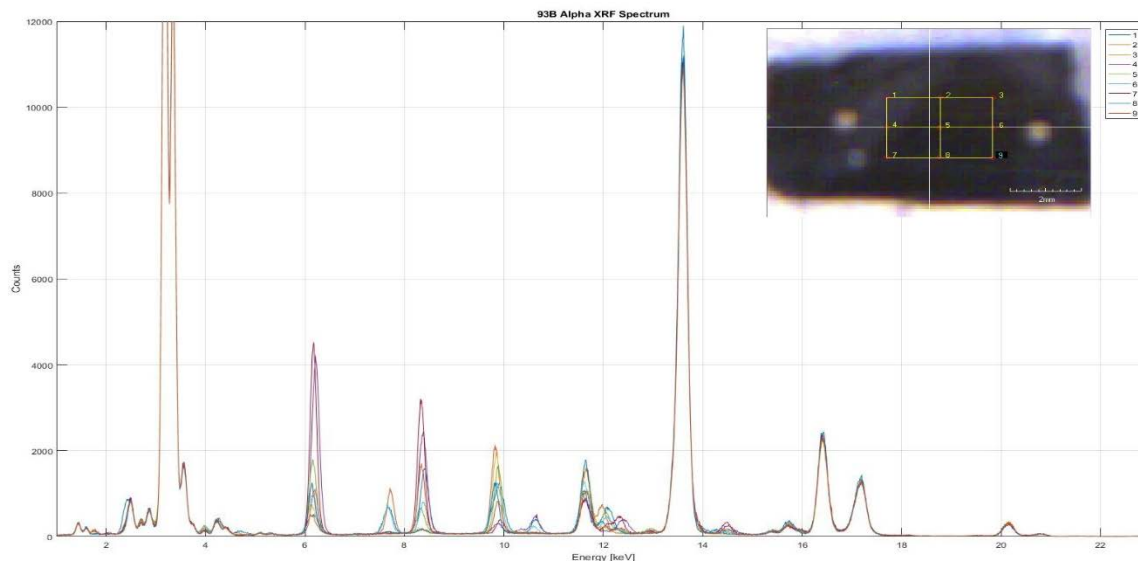


Figure 56. XRF spectra of UO₂-T-93B (α)

Table 20. Elemental composition of UO₂-T-93B (α) via XRF (atomic percent)

	Mg	Si	Ge	As	Zr	Rh	Pd	I	Cs	La	Ce	Gd	Er	Tm	Lu	W	Hg	Pb	Rn	Fr	Ra	Ac	Th	U	Total
Spot 1		0.61	2.19		1.60	2.77	2.00		0.21	0.29			0.08	0.08	2.16	5.40	1.16	0.26	0.24	1.23			0.14	79.59	100.00
Spot 2			4.59		2.42	3.01		0.31	0.19				0.02	0.05	1.48	0.20			2.39	0.88			0.36	84.10	100.00
Spot 3			4.80		2.61	1.74					0.07	1.20	0.05	0.03		0.15			0.54	0.57				88.24	100.00
Spot 4			0.50		0.91	3.57								0.01	0.14	4.36			1.34		1.18	0.09	0.02	87.89	100.00
Spot 5			4.61		2.37	1.51							0.05	0.05		0.25			3.04	1.08			0.65	86.39	100.00
Spot 6			3.23	0.26	2.22	2.34		1.04					0.01	0.03	1.53	2.71			1.52	0.66				84.45	100.00
Spot 7			0.27			0.37							0.04	0.05		3.51	0.15		2.20		1.47			91.95	100.00
Spot 8			2.36		3.34	0.77							0.01	0.04	0.34				3.09	0.23	0.05			89.77	100.00
Spot 9	0.62	0.56	2.22			0.34							0.01	0.05		3.52			2.91	0.20	0.37			89.21	100.00
Maximum	0.62	0.61	4.80	0.26	3.34	3.57	2.00	1.04	0.21	0.29	0.07	1.20	0.08	0.08	2.16	5.40	1.16	0.26	3.09	1.23	1.47	0.09	0.65	91.95	
Minimum	0.62	0.56	0.27	0.26	0.91	0.34	2.00	0.31	0.19	0.29	0.07	1.20	0.01	0.01	0.14	0.15	0.15	0.26	0.24	0.20	0.05	0.09	0.02	79.59	

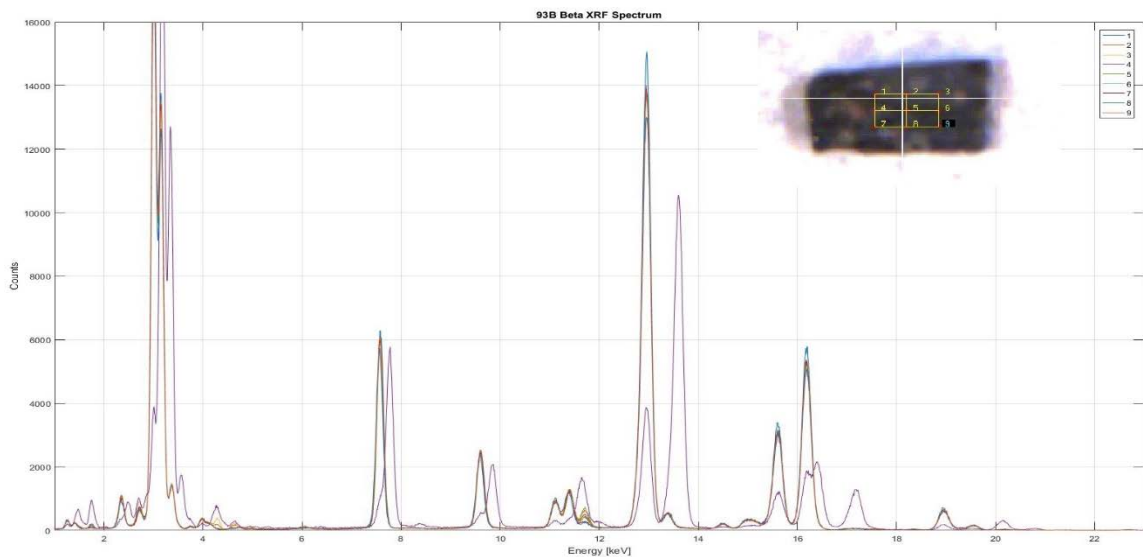


Figure 57. XRF spectra of UO₂-T-93B (β)

Table 21. Elemental composition of UO₂-T-93B (β) via XRF (atomic percentage)

	Mg	Al	Si	S	Ca	Fe	Ge	Rb	Y	Tc	Rh	Sn	Te	Cs	La	Gd	Er	Lu	W	Au	Pb	At	Rn	Fr	Th	U	Total
Spot 1	33.01		0.23	0.68				1.16	0.45	0.74	1.73	2.47	0.48				0.02	0.79		0.33		0.39			57.52	0.01	100.00
Spot 2	25.24		0.59	0.41	0.08			1.49	0.44	0.77	3.65		0.64	0.78	0.30		0.03			0.39	0.01	0.72	0.77		63.69	0.01	100.00
Spot 3	31.23		0.47		0.17			1.36	0.40	0.70	3.46		0.44	2.15			0.01			0.34		0.49			58.77	0.01	100.00
Spot 4	27.00	5.45	4.04			0.07	2.18				4.60			2.45	0.11				0.20				1.07	0.20	13.18	39.47	100.00
Spot 5	31.45		0.88		0.10			1.22	0.55	0.68	2.26		0.48			0.24				0.39		0.40	0.69		60.65	0.01	100.00
Spot 6	28.27		0.74		0.16			1.40	0.44	0.68	1.74		0.59			0.09				0.40		0.54	0.57		64.37	0.01	100.00
Spot 7	8.82			1.67	0.22			1.63	0.80	1.02	2.44		0.55				0.02			0.44		0.76	0.23		81.38	0.01	100.00
Spot 8	24.10	0.52	1.37	0.73	0.28			1.49	0.74	0.94	3.99		0.55									1.29			63.87	0.12	100.00
Spot 9	8.63		1.13	0.64	0.25			1.87	0.73	0.82	2.44		0.71							0.49	0.01	0.55	0.54		81.18	0.01	100.00
Maximum	33.01	5.45	4.04	1.67	0.28	0.07	2.18	1.87	0.80	1.02	4.60	2.47	0.71	2.45	0.30	0.24	0.03	0.79	0.20	0.49	0.01	1.29	1.07	0.20	81.38	39.47	
Minimum	8.63	0.52	0.23	0.41	0.08	0.07	2.18	1.16	0.40	0.68	1.73	2.47	0.44	0.78	0.11	0.09	0.01	0.79	0.20	0.33	0.01	0.39	0.23	0.20	13.18	0.01	

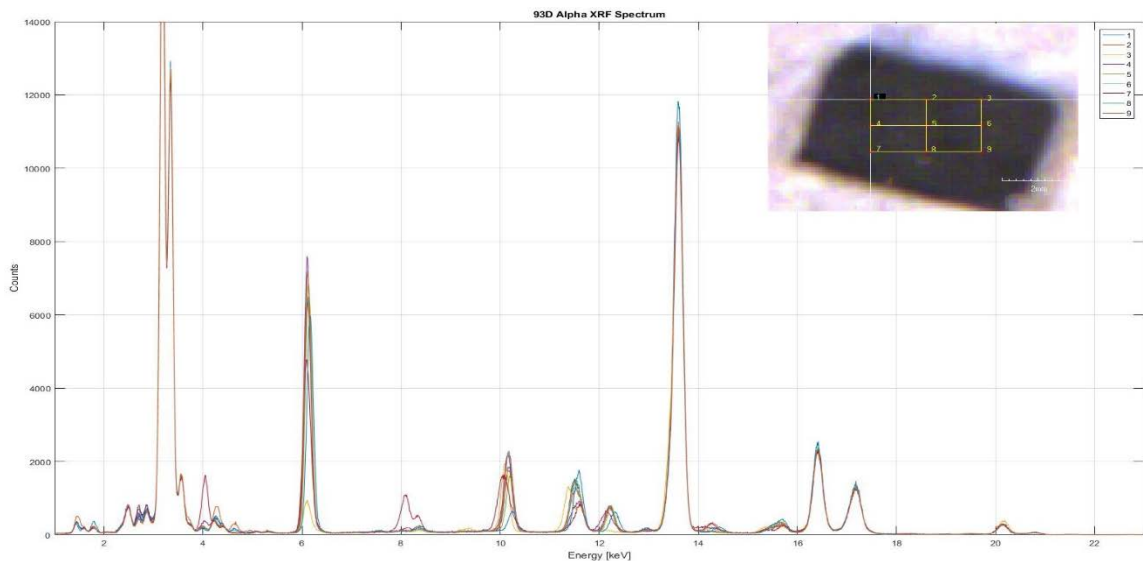


Figure 58. XRF spectra of UO₂-T-93D (α)

Table 22. Elemental composition of UO₂-T-93D (α) via XRF (atomic percentage)

	Al	K	Sc	Ni	Cu	Sr	Zr	Tc	Rh	Pd	Cs	La	Gd	Er	Tm	Ta	W	Pt	Au	Hg	Tl	At	Rn	Fr	Ra	Th	U	Total
Spot 1					0.06		1.13		6.05		1.59	0.19		0.08	0.08		0.35		0.11		1.01	2.96				0.09	86.30	100.00
Spot 2									0.31		4.95	0.37			0.01		0.37				0.80	3.53				0.23	89.43	100.00
Spot 3					0.12	0.10			1.28				1.26	0.05		0.03	0.21	0.11				4.26	0.09				92.48	100.00
Spot 4					0.23			0.37	7.01				1.86	0.06	0.05	0.38	0.36				0.78					0.65	88.24	100.00
Spot 5				0.12			1.40		2.31					0.01	0.05		0.46				3.27	2.37				0.17	89.85	100.00
Spot 6					0.12				0.34	1.51			1.92	0.06			0.40				1.00	3.16				0.09	91.39	100.00
Spot 7		1.42	4.13		1.74	0.49			6.54				2.18		0.01	0.78	0.23			3.06	0.97		0.03	0.04			78.39	100.00
Spot 8							2.76		4.28		0.80	0.17			0.02		0.64		0.13		2.10				0.66	0.61	87.85	100.00
Spot 9	7.70				0.03				0.46				1.77	0.05			0.46				1.07	2.67					85.79	100.00
Maximum	7.70	1.42	4.13	0.12	1.74	0.49	2.76	0.37	7.01	1.51	4.95	0.37	2.18	0.08	0.08	0.78	0.64	0.11	0.13	3.06	3.27	4.26	0.09	0.04	0.66	0.65	92.48	
Minimum	7.70	1.42	4.13	0.12	0.03	0.10	1.13	0.37	0.31	1.51	0.80	0.17	1.26	0.01	0.01	0.03	0.21	0.11	0.11	3.06	0.78	2.37	0.03	0.04	0.66	0.09	78.39	

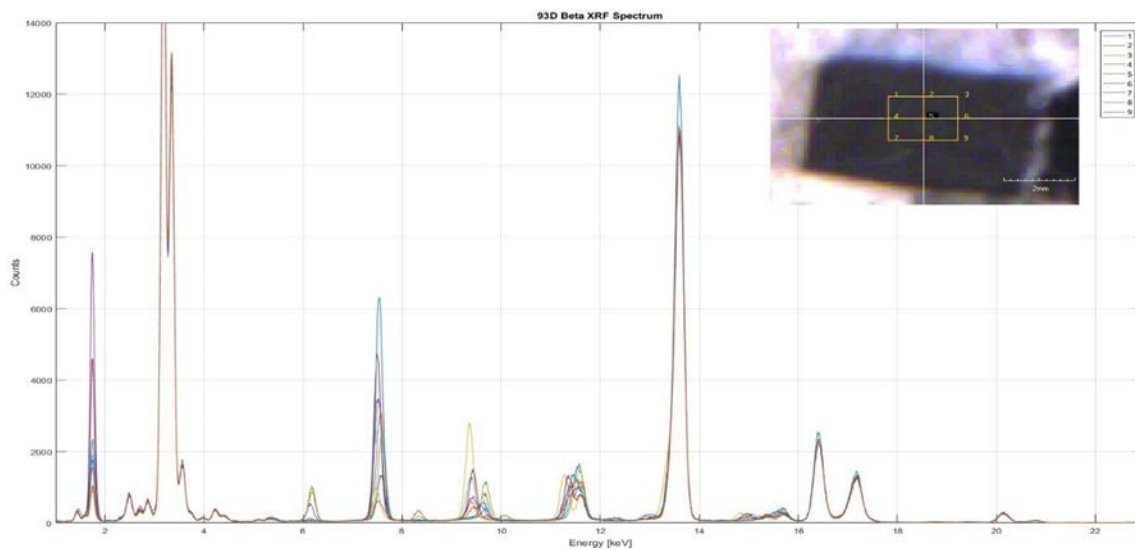


Figure 59. XRF spectra of UO₂-T-93D (β)

Table 23. Elemental composition of UO₂-T-93D (β) via XRF (atomic percentage)

	Mg	Al	Si	K	Cr	Ni	Se	Y	Zr	Rh	Pd	Pr	Lu	W	Pt	Au	At	Rn	Ra	Ac	Th	U	Total
Spot 1	6.25		15.70			0.62			1.51	1.30			1.48	0.04		0.82			0.10		0.06	72.11	100.00
Spot 2			14.27	3.86	0.17	2.98			1.49	1.79	1.85	0.14		0.04	1.14	2.16	1.92			0.04		68.15	100.00
Spot 3			9.64	3.75	0.27	2.46	0.88	1.04	1.28	3.00		0.12			2.04			0.53				75.00	100.00
Spot 4			47.50		0.06	4.62		0.37		2.18	0.71				1.24	0.33	2.03				0.32	40.63	100.00
Spot 5			11.05			0.40			2.59	1.12			1.79	0.24		3.61		0.57	0.37			78.27	100.00
Spot 6	6.65		18.27		0.18	3.58		0.44	1.26	1.48					2.22	0.66	1.41				0.00	63.85	100.00
Spot 7	2.90		32.91		0.17	8.75		0.88		0.92					2.17		2.95	0.41		0.02		47.92	100.00
Spot 8			21.38		0.24	9.87			0.73	1.05						0.34	2.43				0.12	63.85	100.00
Spot 9		1.86	8.67	2.56		1.07			1.81	1.31	2.22			0.72	1.39	0.25	2.98	0.70	0.30			74.16	100.00
Maximum	6.65	1.86	47.50	3.86	0.27	9.87	0.88	1.04	2.59	3.00	2.22	0.14	1.79	0.72	2.22	3.61	2.98	0.70	0.37	0.04	0.32	78.27	
Minimum	2.90	1.86	8.67	2.56	0.06	0.40	0.88	0.37	0.73	0.92	0.71	0.12	1.48	0.04	1.14	0.25	1.41	0.41	0.10	0.02	0.06	40.63	

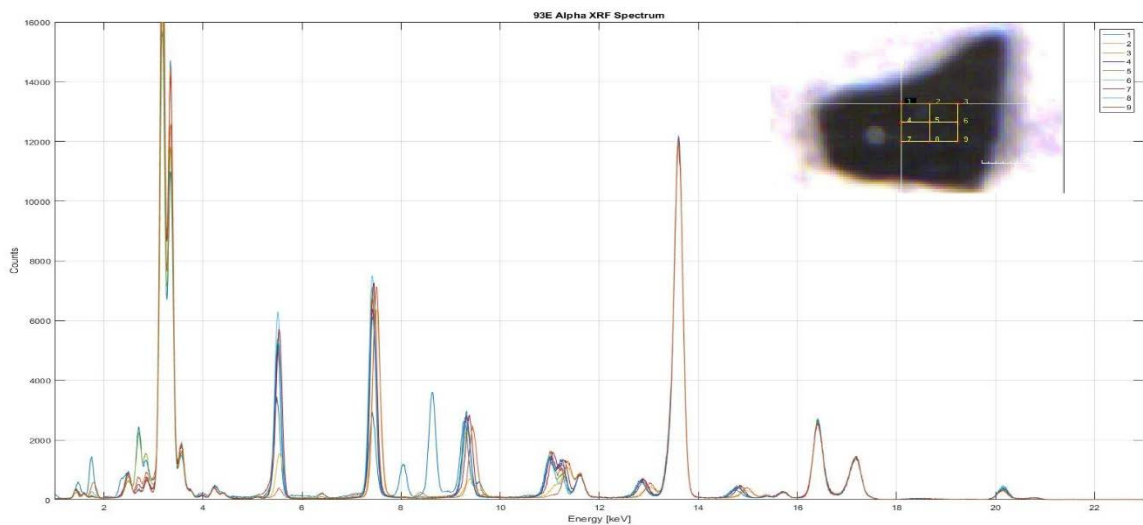


Figure 60. XRF spectra of $\text{UO}_2\text{-T-93E } (\alpha)$

Table 24. Elemental composition of $\text{UO}_2\text{-T-93E } (\alpha)$ via XRF (atomic percentage)

	Mg	Si	Fe	Ge	Br	Kr	Sr	Zr	Ba	Pr	Gd	Tb	Er	Tm	Lu	W	Au	Hg	Rn	Fr	Ra	Ac	U	Total
Spot 1		0.35		3.12									0.04	0.01				4.39		0.05			92.04	100.00
Spot 2		0.53		2.69				0.10					0.03	0.08	1.61	0.58			3.17	1.26	0.51		89.44	100.00
Spot 3		0.39		5.62		0.14	0.16		0.11	0.10			0.03	0.05		0.91				0.58			91.91	100.00
Spot 4		0.93		4.70	3.07	0.02					0.01			0.01					1.56	0.05			89.64	100.00
Spot 5		0.30		2.42	0.72			2.80			0.20				2.14				1.80	0.05			89.57	100.00
Spot 6		0.56		6.27		0.07	0.42			0.02			0.01	0.01		0.12				0.55			91.97	100.00
Spot 7	6.12	0.13	0.11	2.79	3.22		0.40			0.01					2.63	0.18			0.31	0.30			83.80	100.00
Spot 8		0.82		1.81	2.05			0.35	0.10	0.08				0.01	2.07	0.24	5.33		0.28	0.28			86.60	100.00
Spot 9		0.38		0.55				0.09				5.01	0.01		1.05	5.63			0.19	0.25		0.02	86.82	100.00
Maximum	6.12	0.93	0.11	6.27	3.22	0.14	0.42	2.80	0.11	0.10	0.20	5.01	0.04	0.08	2.63	5.63	5.33	4.39	3.17	1.26	0.51	0.02	92.04	
Minimum	6.12	0.13	0.11	0.55	0.72	0.02	0.16	0.09	0.10	0.01	0.01	5.01	0.01	0.01	1.05	0.12	5.33	4.39	0.19	0.05	0.51	0.02	83.80	

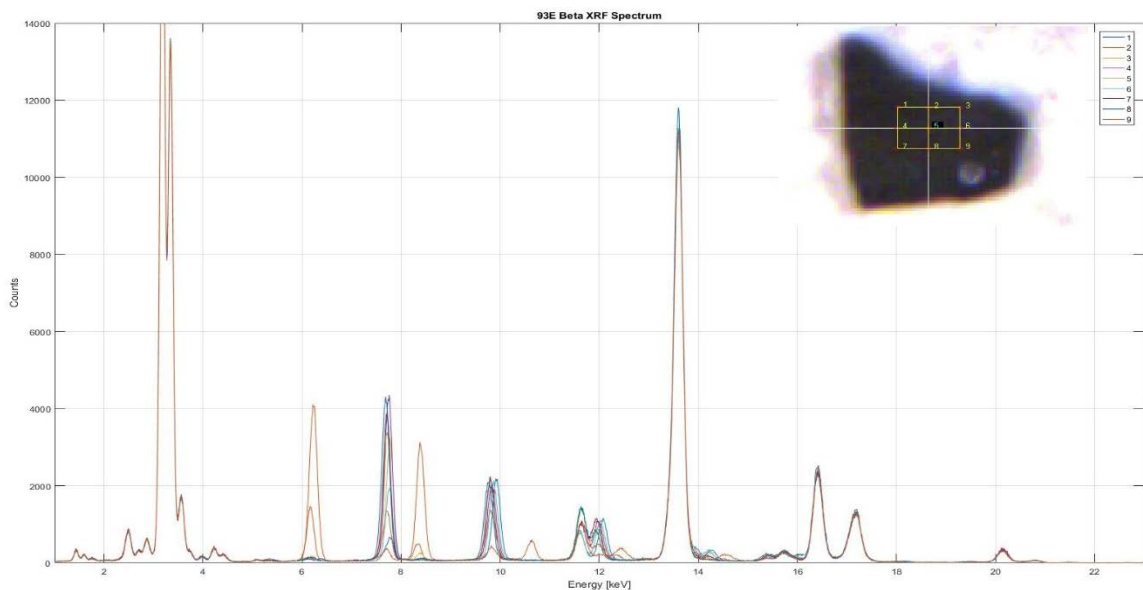


Figure 61. XRF spectra of $\text{UO}_2\text{-T-93E}$ (β)

Table 25. Elemental composition of $\text{UO}_2\text{-T-93E}$ (β) via XRF (atomic percentage)

	Al	Si	K	Fe	Ni	Cu	Zn	Ga	Se	Kr	Y	Zr	Rh	Pd	I	Cs	Ba	Ce	Pr	Er	Tm	Yb	Pt	Au	At	Rn	Ac	Th	U	Total
Spot 1	6.01	9.24	2.28	0.33	3.26	2.00	6.19	3.50	0.99			0.80	16.93		0.52														47.96	100.00
Spot 2				0.48	8.82	0.01	0.01						0.52	5.69						0.11	0.45	9.98						1.56	72.35	100.00
Spot 3		0.40			15.47						1.09						0.18		0.13	0.01			1.18	0.15	2.52	0.02		0.52	78.32	100.00
Spot 4		0.29			12.46			3.55	0.88	0.11	0.49	0.05					0.08						1.66			0.01		0.29	80.14	100.00
Spot 5		0.88		0.07	9.65			1.90					17.09	1.50			0.11		0.03		0.06	5.17	1.76			0.01			61.78	100.00
Spot 6		0.29			13.88			2.85				0.05					0.08		0.17		0.44		2.28						79.96	100.00
Spot 7					15.03						1.59	0.20	3.96	3.07			0.08		0.02	0.04	0.05		3.00			0.29	0.19	0.63	71.84	100.00
Spot 8		0.28						3.61	0.39		0.42	0.02				0.92			0.02		0.08		2.10			0.17	0.09		80.39	100.00
Spot 9		0.44			13.58						1.77							0.10	0.14				4.36		3.22	0.14	0.06	2.88	73.31	100.00
Maximum	6.01	9.24	2.28	0.48	15.47	2.00	6.19	3.61	0.99	0.11	1.77	0.80	17.09	3.07	0.52	0.92	0.18	0.10	0.17	0.11	0.45	9.98	4.36	0.15	3.22	0.29	0.19	2.88	80.39	
Minimum	6.01	0.28	2.28	0.07	3.26	0.01	0.01	1.90	0.39	0.11	0.42	0.02	3.96	1.50	0.52	0.92	0.08	0.10	0.02	0.01	0.05	5.17	1.18	0.15	2.52	0.01	0.06	0.09	47.96	

Table 26. Elemental composition of $\text{UO}_2\text{-T-93B}$ (α) via XRF (atomic percentage) (post PL)

	K	Zn	Ge	As	Kr	Zr	Rh	Nd	Sm	Gd	Tb	Er	Lu	W	Hg	Tl	Pb	Rn	Fr	Ra	Ac	Th	U	Total
Spot 1	2.62		2.58				2.17							1.55	0.34		0.12	0.32					90.29	100.00
Spot 2	6.12						1.60							0.14		0.18		3.12		0.73			88.11	100.00
Spot 3			1.32				1.57	0.16					0.94	0.62				1.98		0.58		0.01	92.81	100.00
Spot 4			1.38				1.80				0.15		2.60	4.11	2.45		0.21		0.59			0.05	86.66	100.00
Spot 5		0.02	2.28			2.42	2.38			1.35		0.06		0.41				2.43				0.46	88.19	100.00
Spot 6	6.19			0.12										2.88		0.54		0.60		1.35			88.32	100.00
Spot 7	2.08			2.95					0.06		2.34			1.91						0.08			90.58	100.00
Spot 8	3.30		1.43											0.43				0.49					94.34	100.00
Spot 9			0.12		0.08	2.20				1.34								0.51					95.75	100.00
Maximum	6.19	0.02	2.58	2.95	0.08	2.42	2.38	0.16	0.06	1.35	2.34	0.06	2.60	4.11	2.45	0.54	0.21	3.12	0.59	1.35	0.08	0.46	95.75	
Minimum	2.08	0.02	0.12	0.12	0.08	2.20	1.57	0.16	0.06	1.34	0.15	0.06	0.94	0.14	0.34	0.18	0.12	0.32	0.59	0.58	0.08	0.01	86.66	

**Table 27. Elemental composition of UO₂-T-93D (α) via XRF (atomic percentage)
(post PL)**

	Al	Si	K	Fe	Ni	Cu	Ga	Ge	Se	Sr	Rh	I	Cs	Gd	Er	Lu	Hf	Ta	W	Au	Hg	At	Rn	Fr	Th	U	Total
Spot 1			4.97		0.55	0.54				0.45	2.60			2.03	0.04				0.03		2.79	2.58	0.05	0.05		83.32	100.00
Spot 2			5.78	0.96							1.01			1.78	0.01						1.54	4.26	0.65			84.02	100.00
Spot 3		2.92							1.17		10.00		5.41					0.97	0.67		0.70	1.37			5.15	71.65	100.00
Spot 4					0.39	0.33	2.14	0.61	2.84		3.80	2.66		0.35			0.77		0.17		1.94					84.01	100.00
Spot 5		2.70			0.88						2.12					0.59				0.44		2.69			0.61	89.98	100.00
Spot 6					0.32						6.09			0.92				1.89				2.38	0.37			88.04	100.00
Spot 7																										0.00	
Spot 8											0.65			1.47					0.28		2.28	3.49	0.14			91.70	100.00
Spot 9	6.26	5.56			1.40	0.89					4.18			0.44		1.51		0.48		0.57		4.38				74.33	100.00
Maximum	6.26	5.56	5.78	0.96	1.40	0.89	2.14	0.61	2.84	0.45	10.00	2.66	5.41	2.03	0.04	1.51	0.77	1.89	0.67	0.57	2.79	4.38	0.65	0.05	5.15	91.70	
Minimum	6.26	2.70	4.97	0.96	0.32	0.33	2.14	0.61	1.17	0.45	0.65	2.66	5.41	0.35	0.01	0.59	0.77	0.48	0.03	0.44	0.70	1.37	0.05	0.05	0.61	71.65	

Appendix C

Table 28. 93B PL peaks from spot 1 (all peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	184.0	19357.8	3635.2	27508.8
2	70.3	25105.8	3708.3	26966.5
3	218.4	172761.3	3926.3	34172.8
4	128.9	407610.5	4148.6	24104.5
4	239.7	592568.8	4401.1	22721.6
6	325.3	335085.7	4719.0	21190.9
7	276.4	86524.3	5026.1	19896.1
8	309.8	71491.5	5218.4	19163.0
9	182.6	27143.1	5456.3	18327.4
10	147.9	21153.5	5646.6	17709.8
11	291.1	27485.5	5870.7	17033.7
12	173.3	7667.9	6042.0	16550.8
13	250.1	7823.1	6217.8	19165.2

Table 29. 93B PL peaks at spot 2 (all peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	139.1	37472.6	3610.9	27693.9
2	62.5	37442.8	3706.7	26978.2
3	316.4	304239.9	3850.3	25972.0
4	374.4	447004.9	4086.2	24472.6
5	351.2	328412.3	4344.9	23015.5
6	248.7	115621.9	4588.9	21791.7
7	249.5	118534.4	4772.4	20953.8
8	207.8	74600.7	4984.9	20060.6
9	273.6	74322.7	5198.9	19234.8
10	245.7	18002.4	5617.3	17802.1
11	421.9	23720.5	5899.8	16949.7
12	215.1	27137.1	5423.8	18437.3

Table 30. 93B PL peaks at spot 3 (green peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	350.1	1.01119E7	3641.4	27462.0
2	350.4	9.16452E6	3926.3	25469.3
3	352.8	4.25926E6	4143.1	24136.5
4	496.4	4.14295E6	4420.4	22622.4
5	523.2	1.98945E6	4744.6	21076.6
6	193.5	302723.3	5012.9	19948.5
7	308.6	547824.9	5203.6	19217.5
8	288.7	237326.9	5456.6	18326.4
9	491.6	251089.2	5639.4	17732.4
10	826.5	588918.3	6044.4	16544.2

Table 31. 93B PL peaks at spot 4 (green peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	350.2	4.67374E6	3654.3	27365.0
2	331.2	3.74885E6	3932.4	25429.7
3	343.2	1.99173E6	4147.8	24109.2
4	458.4	1.68369E6	4392.8	22764.5
5	458.5	848011.4	4733.1	21127.8
6	157.6	100263.7	5025.8	19897.3
7	272.3	112071.3	5202.7	19220.8
8	229.9	171392.1	5468.3	18287.2
9	212.8	156838.8	5631.6	17756.9
10	248.3	148805.3	5755.3	17375.3
11	129.0	70766.4	5900.0	16949.2
12	137.8	61447.2	6019.8	16611.8
13	128.2	10494.5	6222.5	16070.7

Table 32. 93B PL peaks a spot 5 (green peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	166.7	3608.3	3608.3	27713.9
2	74.9	9356.2	3711.3	26944.7
3	322.9	93820.0	3921.9	25497.8
4	173.7	66747.4	4147.8	24109.2
5	306.2	145414.4	4400.4	22725.2
6	411.6	141143.7	4731.6	21134.5
7	228.4	39498.6	5020.9	19916.7
8	191.4	30997.3	5213.1	19182.4
9	260.3	33114.2	5435.5	18397.6
10	247.2	17409.6	5645.0	17714.8
11	251.9	14506.6	5798.9	17244.6
12	242.8	11702.7	6030.1	16583.5
13	201.9	5550.0	6200.2	16128.5

Table 33. 93D PL peaks at spot 1 (green peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	328.6	144313E6	3662.8	27301.5
2	39.5	1.83345E6	3929.3	25449.8
3	413.3	1.09524E6	4144.4	24128.9
4	523.4	1.03087E6	4416.1	22644.4
5	521.2	557076.6	4749.2	21056.2
6	290.5	156862.8	5020.8	19917.1
7	269.9	113240.6	5234.1	19105.5
8	281.9	88038.2	5471.9	18275.2
9	226.1	35538.8	5796.3	17252.4

Table 34. 93D PL peaks at spot 2 (green peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	330.7	3.76522E6	3662.4	27304.0
2	419.6	5.60847E6	3911.8	25563.7
3	344.3	1.64488E6	4150.3	24094.6
4	457.6	1.69461E6	4411.6	22667.5
5	475.6	900921.2	4733.4	21126.6
6	310.1	216306.3	5010.1	19959.7
7	474.2	426440.8	5234.1	19105.5
8	204.3	47546.4	5632.6	17753.8

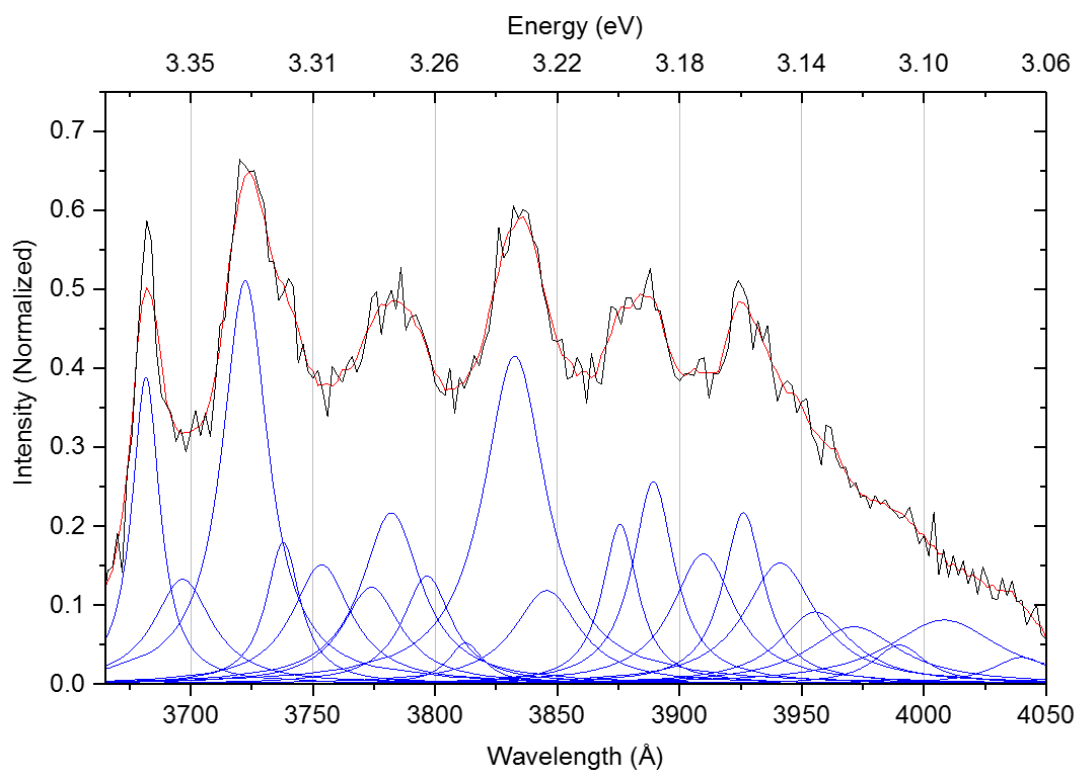


Figure 62. 93B PL spectrum from spot 3 (blue peaks – normalized, subtracted baseline, smoothed)

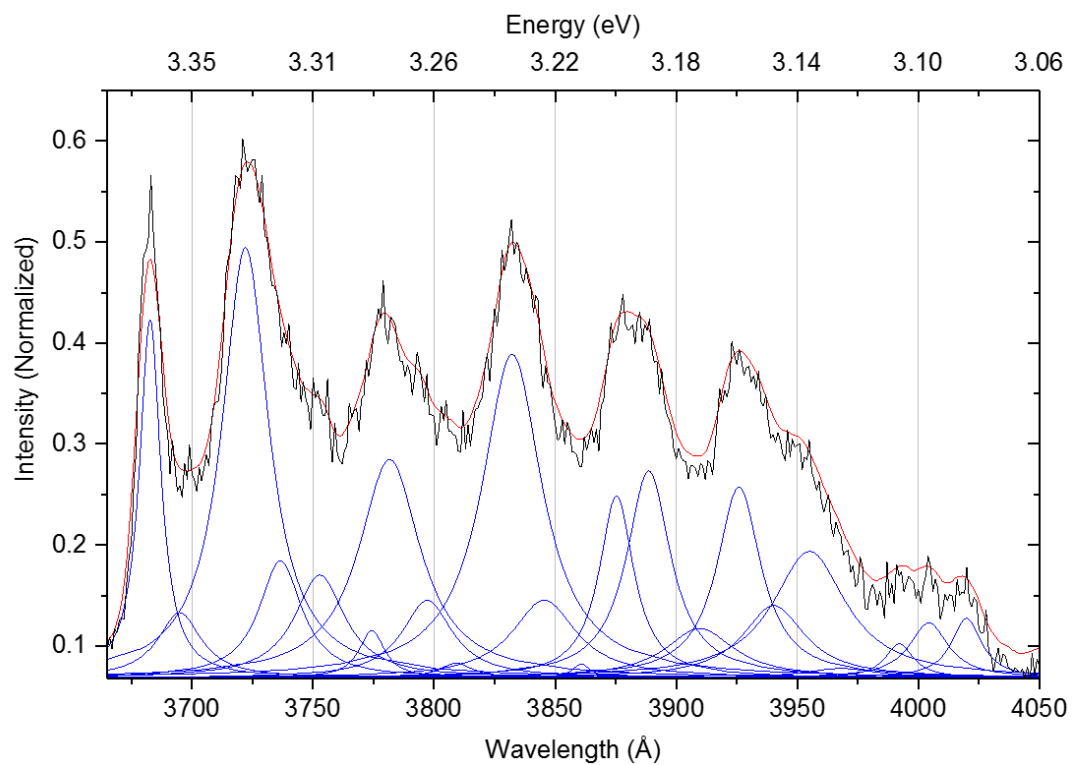


Figure 63. 93B PL spectrum at spot 4 (blue peaks – normalized, subtracted baseline, smoothed).

Table 35. 93B peak distribution (blue peaks)

Peak	Spot 3				Spot 4			
	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	13.8	7.8	3681.7	27161.4	10.6	5.5	3682.7	27154.0
2	29.1	5.4	3696.7	27051.2	21.9	2.00	3694.9	27064.3
3	22.7	17.1	3722.3	26865.1	23.3	14.5	3722.1	26866.6
4	16.9	4.6	3737.8	26753.7	21.5	3.7	3736.6	26762.3
5	29.6	6.6	3753.6	26641.1	25.5	3.8	3752.8	26646.8
6	29.3	5.3	3773.9	26497.8	12.8	0.9	3774.3	26495.0
7	29.5	9.5	3782.1	26440.3	30.9	9.9	3781.6	26443.8
8	24.5	5.0	3796.7	26338.7	25.4	2.9	3797.2	26335.2
9	17.7	1.4	3812.5	26229.5	17.1	0.4	3809.1	26252.9
10	31.1	19.3	3832.6	26091.9	30.2	14.4	3832.2	26094.7
11	32.9	5.8	3845.7	26003.1	32.3	3.7	3842.5	26024.7
12	19.8	2.8	3860.9	25900.7	9.4	0.2	3860.8	25901.4
13	17.6	5.5	3875.7	25801.8	17.4	408	3875.3	25804.5
14	20.9	8.1	3889.3	25711.6	22.1	6.9	3888.6	25716.2
15	31.3	7.7	3909.8	25576.8	34.6	2.5	3909.7	25577.4
16	20.4	6.7	3926.2	25469.9	22.0	6.3	3925.9	25471.9
17	35.7	8.0	3941.2	25373.0	31.3	3.3	3940.3	25378.8
18	36.4	4.8	3955.6	25280.6	36.7	6.7	3955.0	25284.5
19	46.6	4.7	3971.3	25180.7	36.9	0.5	3968.2	25200.3
20	26.0	1.9	3989.9	25063.3	14.1	0.7	3992.1	25049.5
21	56.0	5.6	4008.2	24948.9	19.5	1.5	4004.3	24973.2
22	30.0	1.1	4040.0	24752.5	15.1	1.3	4019.9	24876.2

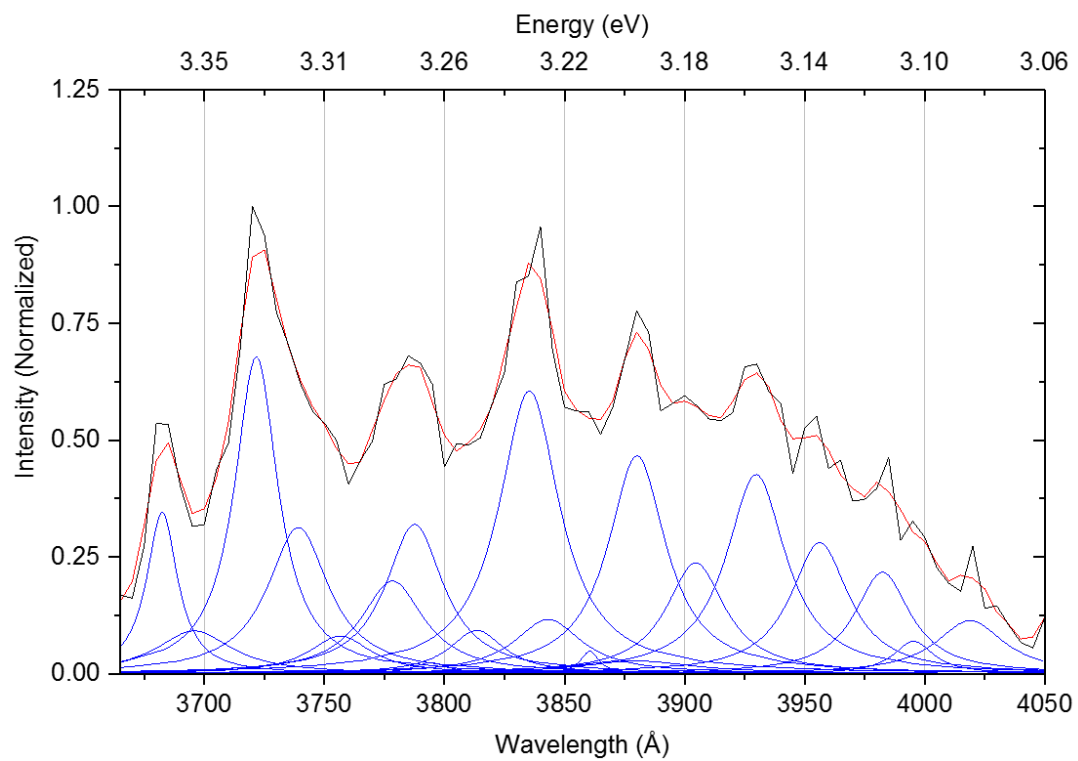


Figure 64. 93D PL spectrum at spot 1 (blue peaks – normalized, subtracted baseline, smoothed).

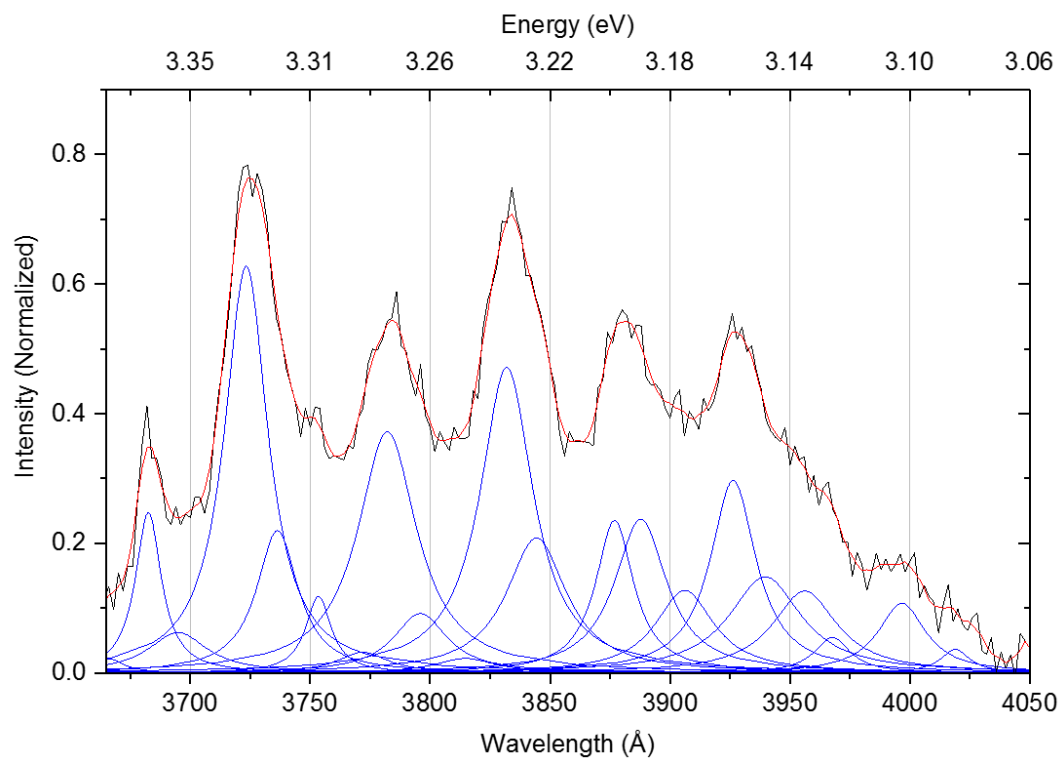


Figure 65. 93D PL spectrum at spot 2 (blue peaks – normalized, subtracted baseline, smoothed)

Table 36. 93D peak distribution (blue peaks)

Peak	Spot 1				Spot 2			
	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	15.7	7.8	3682.4	27156.2	15.0	0.4	3666.3	27275.5
2	38.4	4.7	3695.8	27057.7	13.2	4.8	3682.6	27154.7
3	22.1	22.1	3721.6	26870.2	29.8	2.6	3694.9	27064.3
4	31.1	14.2	3739.1	26744.4	22.1	20.5	3723.3	26857.9
5	31.7	3.8	3756.6	26619.8	21.1	6.9	3736.3	26764.4
6	32.1	9.4	3778.3	26466.9	12.9	2.3	3753.5	26641.8
7	29.5	14.0	3787.6	26401.9	25.7	1.2	3771.9	26511.8
8	17.8	0.6	3794.3	26355.3	29.9	16.6	3782.2	26439.6
9	27.8	3.8	3813.4	26223.3	27.5	3.8	3795.9	26344.2
10	30.8	27.8	3835.4	26072.9	31.0	1.0	3814.8	26213.7
11	34.7	5.9	3843.1	26020.7	26.8	19.0	3831.9	26096.7
12	9.7	0.7	3860.5	25903.4	30.6	9.5	3844.3	26012.5
13	29.3	20.4	3880.2	25771.9	22.7	00.4	3864.5	25876.6
14	29.9	10.6	3904.6	25610.8	19.3	6.9	3876.9	25793.8
15	30.2	19.1	3929.8	25446.6	26.4	9.4	3887.8	25721.5
16	29.7	12.2	3956.3	25276.1	29.7	5.6	3906.1	2560.1
17	28.3	8.9	3982.3	25111.1	23.2	10.4	3926.3	25469.3
18	20.3	2.1	3995.3	25029.4	36.8	7.9	3939.7	25382.6
19	34.6	5.1	4018.8	24883.0	32.9	6.1	3956.2	25276.8
20	-	-	-	-	18.2	1.5	3967.7	25203.5
21	-	-	-	-	24.2	3.7	3996.7	25020.6
22	-	-	-	-	14.9	0.8	4018.9	24882.4

Appendix D

Table 37. 93E PL uranyl peaks at spot 1 (red peaks)

Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	216.0	111060.6	4415.6	22647.0
2	79.1	21520.0	4626.5	21614.6
3	31.0	156214.1	4779.3	20923.6
4	46.2	114906.9	4818.1	20755.1
5	34.4	176206.5	4984.4	20062.6
6	54.5	136274.5	5019.4	19922.7
7	42.4	116848.4	5206.7	19206.0
8	61.1	66680.1	5245.6	19063.6
9	56.2	54137.2	5445.1	18365.1
10	81.2	24084.8	5490.6	18212.9
11	225.9	70704.6	5719.0	17485.6
12	378.7	58312.6	6072.1	16468.8

Table 38. 93E PL peaks at spot 2 U⁴⁺ & uranyl peak distribution (green & red peaks respectively)

U ⁴⁺ Emission Lines					U ⁶⁺ Emission Lines				
Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)	Peak	FWHM (Å)	Area (Counts)	Peak Center (Å)	Peak Center (cm ⁻¹)
1	289.5	632251.2	3658.9	27330.6	1	36.4	104890.9	4779.3	20923.6
2	328.9	1.05818e6	3925.4	25475.1	2	71.4	124405.0	4821.9	20738.7
3	301.8	538667.0	4140.3	24152.8	3	46.3	136012.9	4989.0	20044.1
4	349.5	810122.6	4229.4	23644.0	4	62.4	63701.3	5028.2	19887.8
5	326.6	586306.5	4465.8	22392.4	5	53.9	92722.6	5207.4	19203.4
6	280.9	374768.5	4639.9	21552.2	6	60.1	35342.2	5249.5	19049.4
7	334.6	302520.9	4986.4	20054.5	7	81.3	43087.2	5451.2	18344.6
8	470.4	179350.1	5304.6	18851.6	8	151.9	13364.2	5519.4	18117.9
9	-	-	-	-	9	113.3	18291.3	5716.2	17494.1

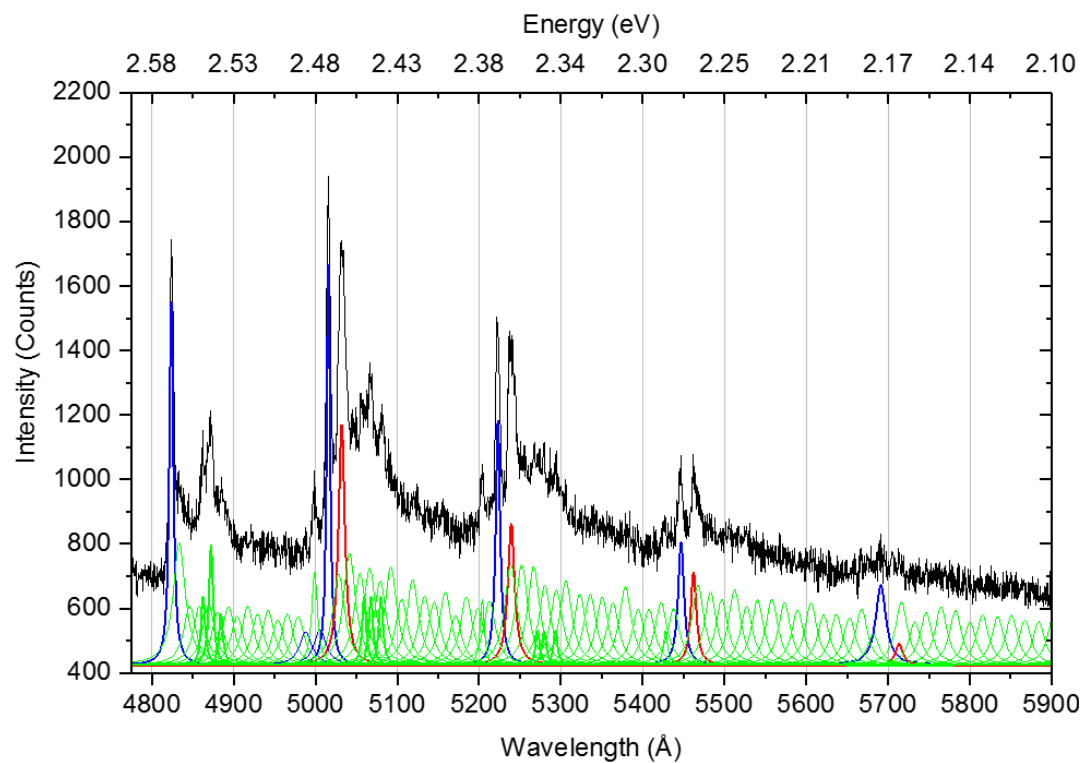


Figure 66. All fitted peaks for 93D spot 3 spectrum

Table 39. Uranyl series F through K in the PL spectrum of 93D

$\nu_{fluorescence} = \nu_f - n_s \nu_s - n_a \nu_a - n_b \nu_b - \sum n_i \nu_i$				
Series F	λ (Å)	ν (cm ⁻¹)	$\Delta \nu_s$ (cm ⁻¹)	$\Delta \nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (1)\nu_i$	4833.37	20689.49	-	41.46
$\nu_f - (1)\nu_s - (1)\nu_i$	5028.32	19887.36	802.13	49.97
$\nu_f - (2)\nu_s - (1)\nu_i$	5238.68	19088.79	798.57	57.29
$\nu_f - (3)\nu_s - (1)\nu_i$	5467.52	18289.82	798.97	69.34
$\nu_f - (4)\nu_s - (1)\nu_i$	5716.26	17493.95	795.87	77.17
Series G	λ (Å)	ν (cm ⁻¹)	$\Delta \nu_s$ (cm ⁻¹)	$\Delta \nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (2)\nu_i$	4846.22	20634.63	-	54.86
$\nu_f - (1)\nu_s - (2)\nu_i$	5041.51	19835.31	799.32	52.05
$\nu_f - (2)\nu_s - (2)\nu_i$	5252.25	19039.48	795.84	49.31
$\nu_f - (3)\nu_s - (2)\nu_i$	5482.87	18238.61	800.87	51.21
$\nu_f - (4)\nu_s - (2)\nu_i$	5732.72	17443.73	794.87	50.22
Series H	λ (Å)	ν (cm ⁻¹)	$\Delta \nu_s$ (cm ⁻¹)	$\Delta \nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (3)\nu_i$	4857.98	20584.67	-	49.9
$\nu_f - (1)\nu_s - (3)\nu_i$	5054.49	19784.39	800.28	50.9
$\nu_f - (2)\nu_s - (3)\nu_i$	5266.69	18987.25	797.14	52.2
$\nu_f - (3)\nu_s - (3)\nu_i$	5496.74	18192.6	794.65	46.0
$\nu_f - (4)\nu_s - (3)\nu_i$	5746.57	17401.68	790.92	42.1
Series I	λ (Å)	ν (cm ⁻¹)	$\Delta \nu_s$ (cm ⁻¹)	$\Delta \nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (4)\nu_i$	4869.40	20536.43	-	48.24
$\nu_f - (1)\nu_s - (4)\nu_i$	5066.12	19738.97	797.46	45.42
$\nu_f - (2)\nu_s - (4)\nu_i$	5280.32	18938.26	800.71	48.99
$\nu_f - (3)\nu_s - (4)\nu_i$	5512.38	18140.99	797.27	51.61
$\nu_f - (4)\nu_s - (4)\nu_i$	5764.79	17346.69	794.3	54.99
Series J	λ (Å)	ν (cm ⁻¹)	$\Delta \nu_s$ (cm ⁻¹)	$\Delta \nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (4)\nu_i$	4880.45	20489.90	-	46.53
$\nu_f - (1)\nu_s - (4)\nu_i$	5079.14	19688.38	801.52	50.59
$\nu_f - (2)\nu_s - (4)\nu_i$	5294.49	18887.56	800.82	50.7
$\nu_f - (3)\nu_s - (4)\nu_i$	5527.02	18092.93	794.63	48.06
$\nu_f - (4)\nu_s - (4)\nu_i$	5782.51	17293.54	799.39	53.15
Series K	λ (Å)	ν (cm ⁻¹)	$\Delta \nu_s$ (cm ⁻¹)	$\Delta \nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (5)\nu_i$	4893.48	20435.35	-	54.55
$\nu_f - (1)\nu_s - (5)\nu_i$	5092.12	19638.21	797.14	50.17
$\nu_f - (2)\nu_s - (5)\nu_i$	5306.07	18846.31	791.9	41.25
$\nu_f - (3)\nu_s - (5)\nu_i$	5540.46	18049.03	797.28	43.9
$\nu_f - (4)\nu_s - (5)\nu_i$	5800.22	17240.73	808.3	52.81

Table 40. Uranyl series L through Q in the PL spectrum of 93D

$v_{fluorescence} = v_f - n_s v_s - n_a v_a - n_b v_b - \sum n_i v_i$				
Series L	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$v_f - (0)v_s - (6)v_i$	4904.15	20390.88	-	44.47
$v_f - (1)v_s - (6)v_i$	5105.31	19587.46	803.42	50.75
$v_f - (2)v_s - (6)v_i$	5323.05	18786.21	801.25	60.1
$v_f - (3)v_s - (6)v_i$	5558.01	17992.05	794.16	56.98
$v_f - (4)v_s - (6)v_i$	5815.42	17195.67	796.38	45.06
Series M	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$v_f - (0)v_s - (7)v_i$	4917.00	20337.59	-	53.29
$v_f - (1)v_s - (7)v_i$	5118.72	19536.14	801.45	51.32
$v_f - (2)v_s - (7)v_i$	5335.79	18741.34	794.8	44.87
$v_f - (3)v_s - (7)v_i$	5573.36	17942.49	798.85	49.56
$v_f - (4)v_s - (7)v_i$	5834.06	17140.74	801.75	54.93
Series N	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$v_f - (0)v_s - (8)v_i$	4929.15	20287.47	-	50.12
$v_f - (1)v_s - (8)v_i$	5133.26	19480.81	806.66	55.33
$v_f - (2)v_s - (8)v_i$	5350.56	18689.58	791.23	51.76
$v_f - (3)v_s - (8)v_i$	5589.35	17891.17	798.41	51.32
$v_f - (4)v_s - (8)v_i$	5850.93	17091.30	799.87	49.44
Series O	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$v_f - (0)v_s - (9)v_i$	4942.00	20234.71	-	52.76
$v_f - (1)v_s - (9)v_i$	5145.06	19436.14	798.57	44.67
$v_f - (2)v_s - (9)v_i$	5363.59	18644.21	791.93	45.37
$v_f - (3)v_s - (9)v_i$	5605.76	17838.78	805.43	52.39
$v_f - (4)v_s - (9)v_i$	5867.39	17043.36	795.42	47.94
Series P	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$v_f - (0)v_s - (10)v_i$	4953.94	20185.95	-	48.76
$v_f - (1)v_s - (10)v_i$	5158.78	19384.44	801.51	51.7
$v_f - (2)v_s - (10)v_i$	5378.87	18591.28	793.16	52.93
$v_f - (3)v_s - (10)v_i$	5621.12	17790.06	801.22	48.72
$v_f - (4)v_s - (10)v_i$	5884.26	16994.49	795.57	48.87
Series Q	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$v_f - (0)v_s - (11)v_i$	4965.53	20138.85	-	47.1
$v_f - (1)v_s - (11)v_i$	5171.10	19338.25	800.6	46.19
$v_f - (2)v_s - (11)v_i$	5394.47	18537.51	800.74	53.77
$v_f - (3)v_s - (11)v_i$	5636.82	17740.49	797.02	49.57
$v_f - (4)v_s - (11)v_i$	5902.82	16941.07	799.42	53.42

Table 41. Uranyl series R through T in the PL spectrum of 93D

$\nu_{fluorescence} = \nu_f - n_s \nu_s - n_a \nu_a - n_b \nu_b - \sum n_i \nu_i$				
Series R	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (12)\nu_i$	4978.76	20085.31	-	53.54
$\nu_f - (1)\nu_s - (12)\nu_i$	5184.51	19288.23	797.08	50.02
$\nu_f - (2)\nu_s - (12)\nu_i$	5407.49	18492.88	795.35	44.63
$\nu_f - (3)\nu_s - (12)\nu_i$	5652.88	17690.09	802.79	50.4
$\nu_f - (4)\nu_s - (12)\nu_i$	5927.08	16871.71	818.38	69.36
Series S	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (13)\nu_i$	4987.99	20048.13	-	37.18
$\nu_f - (1)\nu_s - (13)\nu_i$	5198.39	19236.70	811.43	51.53
$\nu_f - (2)\nu_s - (13)\nu_i$	5422.48	18441.76	794.94	51.12
$\nu_f - (3)\nu_s - (13)\nu_i$	5667.46	17644.6	797.16	45.49
$\nu_f - (4)\nu_s - (13)\nu_i$	5939.67	16835.94	808.66	35.77
Series T	λ (Å)	ν (cm ⁻¹)	$\Delta\nu_s$ (cm ⁻¹)	$\Delta\nu_i$ (cm ⁻¹)
$\nu_f - (0)\nu_s - (14)\nu_i$	5005.55	19977.82	-	70.31
$\nu_f - (1)\nu_s - (14)\nu_i$	5212.72	19183.85	793.97	52.85
$\nu_f - (2)\nu_s - (14)\nu_i$	5437.81	18389.76	794.09	52
$\nu_f - (3)\nu_s - (14)\nu_i$	5682.03	17599.34	790.42	45.26
$\nu_f - (4)\nu_s - (14)\nu_i$	5956.13	16789.43	809.91	46.51

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Vita

Major Steven Hoak commissioned into the United States Army as a Second Lieutenant upon graduating from the United States Military Academy at West Point in 2002. There he earned a Bachelor of Science in Chemical Engineering. As a UH-60 Blackhawk pilot, he served as MEDEVAC and Maintenance Company Platoon Leader while stationed at Fort Wainwright Alaska. There, MAJ Hoak deployed to FOB Echo in support of Operation Iraqi Freedom in 2008 as a MEDEVAC Platoon Leader and pilot.

Following reassignment back to Fort Rucker for the Captains Career Course (CCC), MAJ Hoak commanded Headquarters and Headquarters Company (HHC), 164th Theater Airfield Operations Group (TAOG) before moving back over to TRADOC to serve as a Basic Officer Leadership Course (BOLC) instructor and mentor. In 2014, looking for a more technology/science focused career, Steven made the leap over to the Acquisition Corps. Upon completing entry-level training, Steven was assigned to the Missile Defense Agency as an Assistant Product Manager (APM) in the Terminal High Altitude Area Defense (THAAD) Program Office at Redstone Arsenal, Alabama. MAJ Hoak's next assignment will be as an associate professor at the United State Military Academy teaching systems engineering.

He is the recipient of the Defense Meritorious Service Medal, Meritorious Service Medal, Air Medal, Army Accommodation Medal, and Army Achievement Medal (2). He has completed both Airborne and Air Assault School. Prior to finishing out his Army career, MAJ Hoak would like to serve as a Program Manager for a major defense weapons program, become proficient enough in Russian to take the Defense Language Proficiency Test, and if it is possible, earn a Ph.D. in Nuclear Engineering or a related field. MAJ Hoak has also completed a Master of Business Administration (MBA) from Mississippi State University.

MAJ Hoak is a native of Coal Center, Pennsylvania. He is married to the former Natalya Zidrashko and blessed with three children.

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14. ABSTRACT Single crystal uranium dioxide (UO₂) samples were studied using photoluminescence (PL) to characterize the surface defects present following growth. X-ray Fluorescence (XRF) and gamma ray spectroscopy measurements were collected to help identify any impurities present in the sample. PL measurements were made using a <i>Kimmon Koha Co., LTD.</i> IK series helium-cadmium (HeCd) 325 nm laser with an energy range of 5 mW/10 mV, in a 10⁻⁶ Torr vacuum, and at 10K. Data was collected through a <i>Products for Research Inc. PHOTOCOOL</i>TM series photomultiplier tube (PMT) attached to a <i>Horiba Scientific Inc.</i> SPEX 1250 M monochromator and analyzed with <i>SynerJY</i>TM. Both the emission of U⁴⁺ in UO₂ from 5f¹6d¹→5f² transitions and uranyl emission from surface oxidation was detected. Five 5f¹6d¹→5f² transitions were assigned to peaks at 3.41 ± 0.02, 3.17 ± 0.02, 3.00 ± 0.02, 2.82 ± 0.02, and 2.61 ± 0.01 Å. Six near band edge (NBE) defects were detected and their phonon replicas identified. The uranyl symmetric (797.6 ± 6.1 cm⁻¹), antisymmetric (850.8 ± 7.7 cm⁻¹), bending (171.4 ± 4.4 / 205.3 ± 0.9 / 254.6 ± 1.9 cm⁻¹), and inherent internal defect (50.9 ± 6.6 cm⁻¹) vibrational frequencies are identified for the first time in single crystal UO₂ and in good agreement with other uranyl compounds in literature.					
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