Title: Investigation of Material Property Influenced Stoichiometric Deviations as Evidenced During UV Laser-Assisted Atom Probe Tomography in Fluorite Oxides

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Abstract

Oxide materials are used in numerous applications such as thermal barrier coatings, nuclear fuels, electrical conductors and sensors, all applications where nanometer-scale stoichiometric changes can affect functional properties. Atom probe tomography can be used to characterize the precise chemical distribution of individual species and spatially quantify the oxygen to metal ratio at the nanometer scale. However, atom probe analysis of oxides can be accompanied by measurement artifacts caused by laser-material interactions. In this investigation, two technologically relevant oxide materials with the same crystal structure and an anion to cation ratio of 2.00, pure cerium oxide (CeO_2) and uranium dioxide (UO_2) are studied. It was determined that electronic structure, optical properties, heat transfer properties, and oxide stability strongly affect their evaporation behavior, thus altering their measured stoichiometry, with thermal conductance and thermodynamic stability being strong factors.

Keywords

- Field Evaporation
- Laser-material interactions
- Stoichiometry
- Uranium Dioxide
- Cerium Oxide
- Laser heating

1. Introduction

Oxide based materials are used in a variety of technological applications including nuclear fuel, solid oxide fuel cells (SOFCs), oxygen sensors, catalysts, semiconductors and thermal barrier coatings [1-6]. It has been well documented that the performance of these materials is closely tied to their stoichiometry. For example, stoichiometric deviations in SOFCs can affect the number of oxygen ions available for conduction, thus changing the electron transfer mechanism [7]. Additionally, in nuclear fuels, stoichiometric deviations caused by irradiation-induced defects reduce the effectiveness of heat transport, correlating to a degradation in fuel performance [1]. Thus it is of utmost importance to characterize the precise oxygen to metal (O/M) ratio, especially since it relates directly to oxygen defect behavior [8]. Bulk measurement of stoichiometry is ubiquitous; however, the spatial characterization of stoichiometry at nanometer length scales is problematic. Transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) can both be used to measure stoichiometry, but not without complication. With TEM-EDS, it is difficult to quantitatively measure minute chemical changes [9]. Although TEM-EELS can detect chemical changes at the nanometer scale, the measured electron energy loss intensity is used to infer changes in stoichiometry [9]. Additionally TEM-EELS has low accuracy when characterizing high atomic number elements [9]. Meanwhile spectroscopic techniques, such as secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS), can potentially preferentially sputter specific elements while having very low 3-dimensional resolution [10, 11]. Atom probe tomography (APT) has the unique ability to quantify 3-dimensional chemical changes at the parts-per-million (ppm) level on the nanometer scale, giving it the potential to measure small-scale stoichiometric variations.

APT field evaporates surface ions from a sharp tip of the sample, after which the tip is reconstructed computationally and then subsequently analyzed [12]. While this process is relatively well understood for most conducting materials, especially metallic systems [12], the field evaporation process is not always well controlled for insulating materials [13], leading to artifacts in the measured stoichiometry [14-19]. These can be exacerbated by the presence of a laser used to thermally assist evaporation for oxides and other materials with limited electrical conductivity. Stoichiometric artifacts in oxide materials can significantly complicate the analysis of true chemical deviations in the material, and this study aims to explore the correlation between material properties and evaporation behavior during laser-assisted atom probe analysis.

Recent UV laser-assisted APT results have been published on the evaporation behavior of bulk CeO_2 [20-22]. The results from Kirchhofer et al. [22] indicate that the optimal evaporation behavior of CeO_2 for analysis with APT are obtained using a 1 pJ laser energy, specimen base temperature of 20 K, and a pulse repetition rate of 100 kHz. For UO_2 , it was determined that the optimal conditions for evaporation are a 10 pJ laser energy, specimen base temperature of 50 K, and a pulse repetition rate of 100 kHz [23]. Studies of CeO_2 [22], MgO [24], and Al_2O_3 [24] with APT indicate that correct stoichiometry is only possible at low laser energies for oxides, primarily due to an increase in temperature associated with high laser energies, however, UO_2 differs in this behavior. Low laser energies provide hypostoichiometric chemistries and higher laser energies are needed to achieve laser-assisted evaporation to obtain stoichiometric chemistry. An understanding of this difference in behavior between CeO_2 and UO_2 for analysis with APT is necessary.

CeO₂ and UO₂ have a fluorite crystal structure, and have a similar lattice parameter and melting temperature, as presented in Table 1 [25]. Due to their similarities, CeO₂ is often used as a surrogate material to study the effects of irradiation in oxide nuclear fuels without the additional safety requirements for handling UO₂ [25-27]. In addition, limited atom probe facilities exist that can handle radiological materials. Therefore CeO₂ will be considered often to study irradiation-induced chemical changes with APT.

Analysis of UO₂ using laser-assisted APT is presented and contrasted with CeO₂, specifically using similar instrument conditions to investigate the influence of each material's intrinsic properties. Systematic studies of the evaporation behavior for both CeO₂ [22] and UO₂ [23] will also be used to further elucidate the findings in this study. Although it is generally presumed that the macroscopic behavior of CeO₂ is similar to UO₂, fundamental differences in the electronic structure, optical properties, heat transfer properties, and thermodynamic stability can contribute to dissimilar ionization characteristics. In this study it was observed that the distinct differences in the evaporation behavior between UO₂ and CeO₂ are as a result of complex and compounding UV-laser and material interactions.

Table 1: Comparison of Material Properties

	Lattice Parameter (Å)	Density (g/cm³)	Thermal Conductivity (W/m•K) at 200 K	Thermal Conductivity (W/m•K) at 80 K	Melting Temperature (K)
CeO₂	5.41[28]	7.21[28]	7 [29]	3 [29]	2750 [28]
UO₂	5.47[30]	10.97[31]	12.3[32]	4.9 [32]	3140 [31]

2. Materials and Methods

In this investigation, commercial polycrystalline CeO_2 pellets were obtained from Alfa Aesar, Ward Hill, MA with a grain size of approximately 5 μm and single crystal depleted UO_2 were obtained from the National Research Council, Chalk River Laboratories, Chalk River, Canada. To verify the bulk structure and chemistry of the oxides in this investigation, x-ray diffraction (XRD) was used for CeO_2 and neutron diffraction for UO_2 , respectively. XRD of CeO_2 produced only fluorite-type reflections, with a calculated lattice parameter of 5.407 $\pm$ 0.004, indicating the O/Ce to be 2.00. Neutron diffraction of the UO_2 sample indicates the O/U ratio to be 2.00 $\pm$ 0.001 [33]. Atom probe samples were fabricated by focused ion beam (FIB) techniques with a FEI Quanta 3D FEG FIB and mounted onto an array of Sb micropost [34]. Mounted samples were then annularly milled to a diameter of 70 nm. A CAMECA LEAP 4000X HR atom probe with a UV-laser was used in this investigation. The 355 nm UV-laser has a spot size of approximately 0.5 μm at full-width-half maximum (FWHM) at the specimen surface and pulse duration of <15 ps. For both materials, the UV-laser was used to assist in sample tip evaporation. For UO_2 , the following atom probe run parameters were investigated: 35-50 K tip temperature, 100 kHz, 10-200 pJ and detection rates of 0.003-0.01 atoms/pulse. For UO_2 , tip temperature and detection rate could not be altered significantly to affect its response due to its limited conductivity and brittle nature [35]. Laser energy, however did affect its evaporation behavior with laser energies less than 5 pJ adversely affecting its stoichiometry. Laser energies greater than 10 pJ did not affect the O/U ratio, maintaining an O/U near 2.00. The optimization of run parameters for UO_2 in UV-APT are discussed in detail elsewhere [23]. For CeO_2 , the following atom probe run parameters were investigated: 20-50 K, 100-250 kHz, 2.5-120 pJ, and detection rate 0.01 - 0.03 atoms/pulse. Within these ranges, only a O/Ce ratio less than 2.00, or an

hypostoichiometric ratio, was observed. This indicates that for CeO_2 , the measured stoichiometry using APT within this instrument parameter range will produce a composition that is oxygen deficient. The data presented for both CeO_2 and UO_2 is of 30 K, 120 pJ, 100 kHz, and a detection rate of 0.01 atoms/pulse. At laser energies below 5 pJ, correct stoichiometry will be measured in CeO_2 [22]. However for UO_2 , the laser energy is not sufficient to achieve laser-assisted evaporation since at 5 pJ, the evaporation of ions is primarily controlled by the DC electric field, which produces an oxygen deficient composition measurement [23]. For these reasons, a moderate laser energy of 120 pJ was selected for this comparative study.

3. Results

3.1 Material Chemistry

Data collected from the atom probe was reconstructed using IVAS version 3.6.6 for chemical analysis. Ions detected from atom probe were indexed using their mass-to-charge ratio present in the mass spectrum and used to quantify the sample chemistry. In Fig. 1, the mass spectrums of (a) CeO_2 and (b) UO_2 are presented. In CeO_2 a large peak exists for Ce^{n+} ions, while only a small peak is present for U^{n+} ions, as highlighted with the arrows. In Table 2, the chemistry obtained for CeO_2 and UO_2 was gathered by decomposing the complex ions present in the mass spectrum. The 16 Da peak was assigned as O^+ , as indicated in Fig. 1. However, reassigning the 16 Da peak from O^+ to O_2^{2+} increases the oxygen content only by 0.3 at%. Since only a minute increase in oxygen is measured when assigned as O_2^{2+} , it was left as O^+ . The chemical composition for UO_2 is closer to the ideal oxygen/metal (O/M) ratio of 2.00 than that of oxygen deficient CeO_2 .

Fig. 1: Representative mass spectrum of (a) CeO_2 and (b) UO_2 . Most of the ions detected in CeO_2 are CeO^{n+} , Ce^{n+} , and O_2^+ while for UO_2 the majority are UO_2^{n+} ions.

Table 2: Observed Sample Bulk Chemistry with UV-APT (in at%)

	Ce or U	O	O/Ce or O/U
CeO₂	35.58 +/- 0.01	64.42 +/- 0.01	1.81
UO₂	33.70 +/- 0.01	66.30 +/- 0.02	1.97

3.2 Compositional Variations

Measured stoichiometry is directly dependent on the ion types and corresponding spatial distribution. To evaluate the effect of the incident laser as a function of location along the tip, three small rectangular regions of interest (ROIs) were taken across the diameter of each tip. In Fig. 2, deviation from ideal O/M of 2.00 is plotted for both (a) CeO_2 and (b) UO_2 from the ROIs. For UO_2 , the deviations observed in the ROIs are small, while for CeO_2 there is a greater deviation observed throughout the diameter of tip. This behavior is seen throughout the tip height, indicating that it is not an artifact caused by the initial evaporation of the specimen. The origin of this compositional deviation is the spatial distribution of ion types, shown in top-down hit maps of the tips in Fig. 3 and Fig. 4. A large concentration gradient related to the incident laser is seen in CeO_2 , where the laser side of the tip is rich in O_2^{n+} ions and the opposite side is rich in Ce^{3+} . The three-fold figure that appears in UO_2 is geometrically unrelated to the laser and is due its crystallographic orientation. This artifact is a result of (111) direction normal to the surface and has been observed in literature in other materials [36]. Although not directly

measured, 2D density maps of CeO_2 from Kirchhofer et al. [22] show a similar pattern as in the current results which lead to the observed stoichiometry change in CeO_2 . In the following section, differences in electronic structure, optical properties, thermal conductance properties, and oxide stability will be presented and discussed, as well as possible explanations for these results.

Fig. 2: Variation in composition across tip diameter caused by the laser at the top, center, and bottom of (a) CeO_2 and (b) UO_2 tip. Ions represented as CeO_x and UO_x denotes ions with $x = 1, 2, 3$, or 4 . A negative deviation indicates oxygen deficiency and a positive deviation indicates richness in oxygen.

Figure 3: Top-down ion distribution for majority constituents in the CeO₂ sample.

Figure 4: Top-down ion distribution for majority constituents in the UO₂ sample.

4. Discussion

4.1. Absorption Characteristics

CeO₂ is considered an insulating material with a band gap energy (E_g) of 3.19 eV at room temperature, while UO₂ is a semiconducting material with an E_g of 2.1 eV at room temperature

[37, 38]. However, during atom probe analysis, these materials are both at cryogenic temperature and under an electric field, which affects the band gap energy. Lowering temperature will reduce the E_g of CeO_2 to 2.76 eV and of UO_2 to 2.01 eV, based on density functional theory (DFT) calculations at 0 K [39]. The addition of the standing electric field further reduces the band gap by a variety of mechanisms including the Franz-Keldysh effect, Wannier-Stark localization, and Zener interband tunneling [18, 19]. Further, the accumulation of electronic defects at the surface can enhance laser absorption in this area [40]. CeO_2 has an indirect band gap between the valence and conduction bands [41] which requires the assistance of phonons, or lattice vibrations, for the excitation of electrons to the conduction band [42]. UO_2 , on the other hand, has a direct band gap [43]. Therefore, CeO_2 is not as efficient as UO_2 in transferring electrons from the valence band to the conduction band. Li et al., [20, 21] who previously investigated CeO_2 in atom probe, studied Y and Gd doped CeO_2 , which enhances the material's electrical conductivity and modifies its electronic structure by lowering its band gap energy as compared to pure CeO_2 , improving the electronic properties in UV range [44].

Since CeO_2 and UO_2 have limited electrical conductivity, a pulsed laser is used to thermally evaporate surface ions from the samples investigated. Consequently, there is an additional photonic contribution to the material's behavior under atom probe analysis. Relevant optical properties for CeO_2 and UO_2 are listed in Table 3. For the laser to be strongly absorbed and assist in evaporation of the surface atoms in UV-APT, the wavelength of the laser should be less than or equal to the band gap [42]. With this basic consideration, both CeO_2 and UO_2 are expected to absorb the UV-laser. Next, the absorption behavior of both samples will be considered for a laser with a photon energy of 3.5 eV, calculated from the wavelength of the incident UV laser.

CeO₂ is a good absorber of UV light [45]. UO₂ on the other hand, is only an adequate absorber of UV light with an absorption coefficient (α) of $1.25 \times 10^{-2} \text{ nm}^{-1}$ compared to CeO₂ at the photon energy of the laser. Near uniform illumination of the UV laser is required to maintain data quality in atom probe. The absorption coefficient of CeO₂ was calculated from its dielectric constant (real and imaginary) at the photon energy of the UV-laser. Taking the penetration depth (δ) to be $1/\alpha$; for CeO₂, δ_{CeO_2} is 37 nm and for UO₂, δ_{UO_2} is 80 nm. This indicates that along the tip diameter, CeO₂ will unevenly absorb the UV laser compared to UO₂. This may explain why along the sample side illuminated by the UV laser on CeO₂, its chemistry is near the expected composition and deviates significantly on the opposing side of the tip diameter.

Table 3: Comparison of Specific Optical Properties

	Band gap Wavelength (nm)	Absorption Coefficient (nm⁻¹)	Penetration Depth, δ (nm)
CeO₂	388	2.64×10^{-2} [46]	37
UO₂	590	1.25×10^{-2} [47]	80

The amount of photons absorbed per volume can be calculated using the absorption coefficient to determine the amount of laser intensity, or irradiance, absorbed along the tip. Taking the absorbed laser intensity and considering the same laser energy and intensity on both samples, CeO₂ was determined to have a higher photon absorption density than UO₂. But in CeO₂, an 84% drop in the absorbed photon density across the tip diameter is observed as compared to only a 71% drop in UO₂. This decrease in absorbed photon density across the tip diameter in CeO₂ may be an additional reason why compositional non-uniformity is seen across the tip diameter in CeO₂ as compared to UO₂, although CeO₂ has a higher absorbed photon density than UO₂. This uneven absorption can lead to non-uniform heating across the tip diameter, further affecting the data collected.

4.2. Thermal Conductivity and Diffusivity

The purpose of the UV laser in APT is to thermally assist in the evaporation of surface ions from materials with poor electrical conductivity. Unfortunately, specimen heating will occur with temperatures expected to increase on the order of several hundred Kelvin in oxides [48]. In addition, heat dissipation from the laser is necessary to avoid thermal effects. From the thermal conductivity values listed in Table 1 and for the thermal conductivity values along 30 – 300 K presented in Fig. 5 for both CeO₂ and UO₂, UO₂ will transfer heat better across this temperature regime.

Fig. 5: Comparison of low temperature thermal conductivity between UO₂ [32] and CeO₂ [29] along the expected temperature regime of analysis with UV-APT.

Since the thermal conductivity of CeO₂ is, on average, 40% less than UO₂, it will not dissipate the heat generated between laser pulses as effectively as UO₂. The thermal conductivity of UO₂ peaks at 300 K, a higher temperature than CeO₂ [31]. In addition, the thermal diffusivity at 200 K for CeO₂ and UO₂ is 3.32×10^{-6} and 8.47×10^{-6} m²/s, respectively [49, 50]. For a tip diameter of 80 nm, the expected dissipation time will be 1.93 and 0.76 ns for CeO₂ and UO₂, respectively.

The thermal diffusivity was calculated using the thermal conductivities listed in Table 1 and the specific heat capacities at 200 K of 292.2 and 201.5 Jkg⁻¹K⁻¹ for CeO₂ and UO₂, respectively. The addition of CeO₂ having less thermal conductivity than UO₂ and with its inability to evenly absorb the UV laser efficiently, CeO₂ will likely not evaporate evenly during atom probe analysis, unlike UO₂. Indicating that UO₂ will dissipate heat 2.5 times faster than CeO₂, possibly leading for heat to build-up in CeO₂, between laser pulses. This will cause uneven ion evaporation across the specimen that is present in CeO₂. The addition of CeO₂ dissipating heat slower than UO₂ and with its inability to evenly absorb the UV laser efficiently, CeO₂ will likely not evaporate evenly during atom probe analysis, unlike UO₂. In CeO₂, to mitigate the effects of heating by the laser, very low laser energy is needed to obtain accurate stoichiometry as presented in Fig. 5. UO₂, on the other hand, with a higher thermal conductivity, stoichiometry is not as dependent on laser energy, as presented in Fig. 6, when sufficiently high laser energy is used to achieve laser-assisted evaporation. Not only will the heat transfer properties affect the observed results between CeO₂ and UO₂, but also differences in their stability.

Fig. 6: Effect of laser energy on the O/M ratio in CeO₂ [22] and UO₂ [23]. Constant conditions for UO₂: 50 K, 100 kHz, and a detection rate of 0.003 atoms/pulse.

4.3. Oxide Stability

From the mass spectrum presented in Fig. 1, UO_2 is preferentially evaporated as UO_2^{2+} and UO_2^+ ions, with smaller contributions from the UO^{2+} , UO_3^+ , UO^+ , UO_4^+ , O^+ , O_2^+ , and U^{3+} ions detected. On the other hand, CeO_2 is preferentially evaporated as CeO^{2+} and CeO^+ , with smaller contributions of CeO_2^+ , CeO_2^{2+} , CeO_3^+ , Ce^+ , Ce^{2+} , Ce^{3+} , O_2^+ , and O^+ ions detected. For UO_2 , the majority of ions detected were in the form of complex UO_2^{n+} ($n = 1, 2, 3$) ion types, while for CeO_2 both complex CeO^{n+} ion types and Ce ion types constitute the majority of ions detected. The variation in ion types evaporated can lead to the differences observed in O:Ce/U ratios presented in Table 2. In the case of CeO_2 , the Ce^{4+} ion is not the most stable valence of Ce.[51] Rather, it is Ce^{3+} , which leads to a large hypostoichiometric CeO_{2-x} region in CeO_2 , where oxygen vacancies are created in the fluorite lattice to accommodate the change in the Ce ion charge state [51]. In UO_2 , U^{4+} is not its most stable valence state of uranium, but U^{5+} , leading to hyperstoichiometric UO_{2+x} , caused by the addition of O interstitials inside the fluorite lattice [51]. Of the cerium oxides, Ce_2O_3 is the most stable based on the free energy of oxide formation[52], whereas UO_2 is the most stable of the uranium oxides [53]. Although the ions detected may provide insight into charge/valence of the ions in the sample, it cannot be used to definitively say which ions are present in the CeO_2 and UO_2 lattice.

In a low oxygen partial pressure environment, such as the ultra high vacuum (UHV) chamber of an atom probe, oxide stability can be affected, and is thusly considered. At low oxygen partial pressures, Ce_2O_3 , is more thermodynamically stable than CeO_2 [52]. The removal of oxygen in CeO_2 is favorable and therefore can easily occur in the chamber, without being ionized and

therefore will not be detected and counted, causing oxygen deficient ceria to be measured. This can explain why the majority of the ions detected are of the CeO^{n+} type. In such conditions, the bonding of oxygen in CeO_2 maybe weaker than that of oxygen in UO_2 in the environment of the atom probe chamber. This can be seen as the laser energy in UV-APT plays a significant role in the measured chemistry of CeO_2 , with very low laser energy providing a O:Ce ratio closer to 2.00 since higher electric fields are present which can ionize the escaped oxygen [22]. Since the majority of ions evaporated are UO_2^{n+} , this indicates that the bonding of the U to O in UO_2 is relatively stronger than CeO_2 . Not only is the predominance of these ion types present at 120 pJ, but also the amount increases in both CeO_2 and UO_2 with higher laser energies. The majority of ions detected at high laser energies in CeO_2 are primarily of the CeO^{n+} type [22], while for UO_2 , at laser energies above 200 pJ, over 98% of the ions detected are of the UO_2^{n+} type [23] where a lower electric field is applied [54] and therefore a lower chance of ionizing the escaping oxygen. Only ions emitted by the pulsed laser are detected at higher laser energies.

In Fig. 7, the ion types detected along the concentration gradients across the tip diameter for both CeO_2 and UO_2 are shown. As mentioned above, the primary ion detected for CeO_2 and UO_2 are CeO^{n+} and UO_2^{n+} , respectively. For CeO_2 , the O_2^+ ion is largely responsible for the concentration gradient. At the side of tip illuminated by the UV laser, approximately 30% of the ions detected are O_2^+ and toward the other end of the tip it is dropped to 9%, while the amount of Ce^{n+} ions increase from 0% at the side illuminated by the UV laser to approximately 5% on the opposing side of the sample tip. For UO_2 , there is only a small change in the observed ions types from the side illuminated by the laser to the other end of the sample tip. UO_2^{n+} ion types increase from 83% at the side illuminated by the laser to 94% at the end of the sample tip. In UO_2 , this increase

in UO_2^{n+} ions is followed by a decrease in O^{n+} ions from 5 to approximately 1% and UO^{n+} ions from 10 to 6% from the end illuminated by the laser to the other end, negating any change in the overall chemistry, unlike CeO_2 . This change in ion types in CeO_2 from the side illuminated by the UV laser to the other end of the tip can be attributed to the uneven absorption of the UV in CeO_2 , while for UO_2 it is more evenly absorbed. This uneven absorption of the UV laser will also lead to uneven heating, which will also lead to degradation in the data quality and changes in ion counts and types, as presented in Fig. 7.

Fig. 7: Distribution of ion types evaporated from the side illuminated by the laser of the tip to the other end of the sample tip in (a) CeO_2 and (b) UO_2 where n denotes ions with a charge state of 1, 2, or 3. Arrows indicate corresponding axis for the amount of CeO^{n+} and UO_2^{n+} ions in percentage.

Similar behavior has been observed in literature in undoped CeO_2 investigated in UV-APT and attributed to inhomogeneity of the electric field on the surface of the sample [22]. Modification of the surface by the removal of its specific ions may change the local chemistry, in turn changing the electrical conductivity at the surface by reducing the amount of energy required for electron excitation by reducing the band gap. Localized changes of the electrical conductivity of CeO_2 at the surface will change its evaporation behavior, which could also contribute to the observed localized chemistry change.

5. Conclusions

In conclusion, work was presented comparing the measured chemistry in two fluorite structured oxide materials, cerium oxide and uranium dioxide, as measured with UV laser-assisted APT. Although both materials are expected to have similar O:Ce/U stoichiometry of 2.00 due to the anion and cation ordering within its crystal structure, this was not observed. With APT, the measured chemistry of CeO_2 was oxygen deficient and for UO_2 , the chemistry measured was near the expected stoichiometry of 2.00. Differences in laser absorption, thermal conductance and thermodynamic oxide stability will influence the measured chemistry of these materials and oxides in general with UV-APT. CeO_2 , an insulating material with an indirect band gap, requires the assistance of phonons to absorb the UV-laser energy. UO_2 on the other hand, is a semiconducting material with a direct band gap, requires no additional assistance in absorption of a UV-laser with this specific laser energy, consequently absorbs more effectively than CeO_2 . Due to UO_2 dissipating heat 2.5 times faster than CeO_2 , thermal effects caused by the use of the UV laser will degrade the observed chemistry in CeO_2 as compared to UO_2 . The difference in behavior leads to variations in chemistry along the direction of laser illumination in CeO_2 , which are not observed in UO_2 , and can be attributed to the differences in the absorption coefficient. UO_2 absorbs the UV-laser evenly throughout the tip diameter while CeO_2 only absorbs the UV laser to a calculated depth of 37 nm, smaller than the tip diameter.

Energetically, UO_2 is more stable than CeO_2 due to its lower free energy of oxide formation. CeO_2 in a low oxygen environment tends to lose oxygen and will become hypostoichiometric until enough oxygen is lost that its structure and phase changes to the more stable form of Ce_2O_3 . For UO_2 , it is unfavorable to lose oxygen as easily as CeO_2 in similar conditions. This can be

seen in the results presented, as the measured stoichiometry of CeO_2 was 1.81 as compared to the measured stoichiometry of UO_2 of 1.97. Additionally, CeO_2 stoichiometry as measured with UV-APT varies with laser energy, while the stoichiometry of UO_2 does not, providing further insight into the stabilities of these oxides. For these reasons, not only does the free energy of oxides need to be taken into account but also for carbides, nitrides, and borides to determine whether the actual chemistry measured by UV-APT will be observed.

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