



# Investigation of material property influenced stoichiometric deviations as evidenced during UV laser-assisted atom probe tomography in fluorite oxides



Billy Valderrama<sup>a</sup>, Hunter B. Henderson<sup>a</sup>, Clarissa A. Yablinsky<sup>b</sup>, Jian Gan<sup>c</sup>, Todd R. Allen<sup>b,c</sup>, Michele V. Manuel<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Florida, 100 Rhines Hall, Gainesville, FL 32611, USA

<sup>b</sup> Department of Nuclear Engineering, University of Wisconsin-Madison, 921 ERB, 1500 Engineering Drive, Madison, WI 53706, USA

<sup>c</sup> Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA

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## ABSTRACT

Oxide materials are used in numerous applications such as thermal barrier coatings, nuclear fuels, and 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 ( $\text{CeO}_2$ ) and uranium oxide ( $\text{UO}_2$ ) 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.

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## 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.

\* Corresponding author at: University of Florida, 152 Rhines Hall, Gainesville, FL 32611, USA. Tel.: +1 352 846 3780.

E-mail address: [mmanuel@mse.ufl.edu](mailto:mmanuel@mse.ufl.edu) (M.V. Manuel).

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<sub>2</sub> [20–22]. The results from Kirchhofer et al. [22] indicate that the optimal evaporation behavior of CeO<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> [22], MgO [24], and Al<sub>2</sub>O<sub>3</sub> [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<sub>2</sub> 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<sub>2</sub> and UO<sub>2</sub> for analysis with APT is necessary.

CeO<sub>2</sub> and UO<sub>2</sub> have a fluorite crystal structure, and have a similar lattice parameter and melting temperature, as presented in Table 1 [25]. Due to their similarities, CeO<sub>2</sub> is often used as a surrogate material to study the effects of irradiation in oxide nuclear fuels without the additional safety requirements for handling UO<sub>2</sub> [25–27]. In addition, limited atom probe facilities exist that can handle radiological materials. Therefore CeO<sub>2</sub> will be considered often to study irradiation-induced chemical changes with APT.

Analysis of UO<sub>2</sub> using laser-assisted APT is presented and contrasted with CeO<sub>2</sub>, specifically using similar instrument conditions to investigate the influence of each material's intrinsic properties. Systematic studies of the evaporation behavior for both CeO<sub>2</sub> [22] and UO<sub>2</sub> [23] will also be used to further elucidate the findings in this study. Although it is generally presumed that the macroscopic behavior of CeO<sub>2</sub> is similar to UO<sub>2</sub>, 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 UO<sub>2</sub> and CeO<sub>2</sub> are as a result of complex and compounding UV-laser and material interactions.

## 2. Materials and methods

In this investigation, commercial polycrystalline CeO<sub>2</sub> pellets were obtained from Alfa Aesar, Ward Hill, MA with a grain size of approximately 5 μm and single crystal depleted UO<sub>2</sub> 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<sub>2</sub> and neutron diffraction for UO<sub>2</sub>, respectively. XRD of CeO<sub>2</sub> produced only fluorite-type reflections, with a calculated lattice parameter of 5.407 ± 0.004, indicating the O/Ce to be 2.00. Neutron diffraction of the UO<sub>2</sub> sample indicates the O/U ratio to be 2.00 ± 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-doped Si microposts [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<sub>2</sub>, 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 CeO<sub>2</sub>, 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<sub>2</sub> in UV-APT are discussed in detail elsewhere [23]. For CeO<sub>2</sub>, 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<sub>2</sub>, the measured stoichiometry using APT within this instrument parameter range will produce a composition that is oxygen deficient. The data presented for both CeO<sub>2</sub> and UO<sub>2</sub> 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<sub>2</sub> [22]. However for UO<sub>2</sub>, 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<sub>2</sub> and (b) UO<sub>2</sub> are presented. In CeO<sub>2</sub> a large peak exists for Ce<sup>m+</sup> ions, while only a small peak is present for U<sup>m+</sup> ions, as highlighted with the arrows. In Table 2, the chemistry obtained for CeO<sub>2</sub> and UO<sub>2</sub> was gathered by decomposing the complex ions present in the mass spectrum. The 16 Da peak was assigned as O<sup>+</sup>, as indicated in Fig. 1. However, reassigning the 16 Da peak from O<sup>+</sup> to O<sub>2</sub><sup>2+</sup> increases the oxygen content only by 0.3 at%. Since only a minute increase in oxygen is measured when assigned as O<sub>2</sub><sup>2+</sup>, it was left as O<sup>+</sup>. The chemical composition for UO<sub>2</sub> is closer to the ideal oxygen/metal (O/M) ratio of 2.00 than that of oxygen deficient CeO<sub>2</sub>.

### 3.2. Compositional variations

Measured stoichiometry is directly dependent on the ion types and their corresponding spatial distribution. To evaluate the effect of the incident laser as a function of location along the tip, three

**Table 1**  
Comparison of material properties.

	Lattice parameter (Å)	Density (g/cm <sup>3</sup> )	Thermal conductivity (W/m K) at 200 K	Thermal conductivity (W/m K) at 80 K	Melting temperature (K)
CeO <sub>2</sub>	5.41 [28]	7.21 [28]	7 [29]	3 [29]	2750 [28]
UO <sub>2</sub>	5.47 [30]	10.97 [31]	12.3 [32]	4.9 [32]	3140 [31]

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