

# Wednesday Afternoon, November 8, 2023

## Actinides and Rare Earths Focus Topic Room C124 - Session AC+AS+MI+TH-WeA

### Emerging Topics and Methods in Actinide/Rare Earth Sciences

**Moderators:** Edgar Buck, PNNL, Krzysztof Gofryk, Idaho National Laboratory, Liane Moreau, Washington State University

2:20pm **AC+AS+MI+TH-WeA-1 Chemical Imaging and Applications Using High Energy Resolution Fluorescence Detection for the Actinides, Samuel Webb, N. Edwards, V. Noel**, SLAC National Accelerator Laboratory **INVITED**  
Microscale synchrotron radiation-based x-ray fluorescence (SR-XRF) chemical analyses can provide a unique capability for chemical signature recognition and classification capabilities for actinide micro-particle analysis. SR-XRF is well suited to forensic type analyses of small particles because it is rapid, non-destructive, highly sensitive, has good spatial resolution, and can provide chemical information on the elements that are present when combined with x-ray absorption spectroscopy (XAS). The combination of spatially resolved distribution and chemical information, often known as chemical imaging, effectively provides a “chemical morphology” of the sample of interest and can show how chemical states are distributed within and among a series of particles. This type measurement is critical for understanding particle origin and history, as the spectroscopy, and its spatial distribution, can provide unique and complementary chemical signatures that may not be elucidated with other forms of measurement.

However, the conventional XAS capability in the near edge region as commonly implemented is often inadequate for systems that require high sensitivity or require a higher detail of spectroscopic information. This can be overcome with the combination of traditional micro SR-XRF and XAS, integrated with a high energy resolution fluorescence detector (HERFD) crystal analyzer. This has been recently implemented at BL 6-2b at SSRL and applied in the determination of the micron-scale oxidation state of uranium in particles. A discussion of the image and data processing techniques that can be applied using spatially resolved HERFD to obtain chemical and structural information, as well as the distribution of phases across different particles at the micro-scale, will also be presented.

3:00pm **AC+AS+MI+TH-WeA-3 High Energy X-Ray Characterization of Microstructure at Macroscopic Depths in Pu Alloys, Donald Brown**, Los Alamos National Laboratory; *T. Carver, R. Pokharel*, Los Alamos National Laboratory; *A. Smith, J. Park, P. Kenesei*, Argonne National Laboratory **INVITED**

High energy (95keV) X-rays were utilized to characterize the microstructure of six PuGa alloy samples. The samples had different gallium content, age, and history (i.e. thermos-mechanical processing). The crystallographic textures, phase fractions, lattice parameters and dislocation densities of each sample were evaluated through distinct analysis techniques. The textures of the samples were modest. In each case, the dislocation densities were relatively high, comparable to cold worked metals, with some attributable to mechanical work and some likely due to self-irradiation damage (aging). The lattice parameters determined in the predominantly single-phase samples were larger than expected based on the nominal Ga concentration. The lattice parameter increase is attributed to self-irradiation induced Ga segregation leaving the matrix Ga lean. Finally, measurements of the lattice parameter were completed as a function of temperature to determine the crystallographic thermal expansion of the material.

4:20pm **AC+AS+MI+TH-WeA-7 Native Oxide Growth of Pu—Ga Alloys, Kasey Hanson, S. Hickam, D. Olive, A. Pugmire**, Los Alamos National Laboratory

Plutonium corrosion has proven to be an intricate area of research that garners considerable attention. In particular, understanding plutonium oxidation is significant to the safe handling and storage of plutonium metal, which is known to readily oxidize under ambient conditions. In order to mitigate this, plutonium metal is commonly stored in inert atmospheres. These include gloveboxes as well as ultra-high vacuum (UHV) chambers used for materials characterization.

The objective of this work is to measure oxidation rates of plutonium metal in various storage environments. To achieve this, spectroscopic ellipsometry was selected due to its prevalence in a variety of industries to measure thin-film thickness. A non-destructive technique, ellipsometry exposes the sample to polarized light, and through changes in the amplitude ratio and phase difference of the reflected vs. incident light, one can generate a material's optical properties that can be used to determine oxide thicknesses.

Building upon previous work, this presentation will present the optical constants of plutonium metal, achieved through the use of ion sputtering under UHV, and plutonium oxide formed on plutonium metal in various storage and exposure conditions. These results will then be used to model oxide thickness values directly from ellipsometry measurements as well as provide additional insights into the nature of the oxide films relevant to plutonium storage and handling.

4:40pm **AC+AS+MI+TH-WeA-8 Molecular Beam Epitaxy of Ternary Nitrides: From Transition Metals to Actinoids, Kevin Vallejo**, Idaho National Laboratory; *S. Gutierrez Ojeda*, Universidad Nacional Autonoma de Mexico; *G. Hernandez Cocoltzi*, Benemerita Universidad Autonoma de Puebla, Mexico; *S. Zhou, K. Gofryk, B. May*, Idaho National Laboratory

The exceptional properties of transition metal nitrides for coatings, as well as photo- and electrochemical applications have opened the doors for more detailed studies of their structure and synthesis. Mn- and Cr- nitrides are strong candidates to showcase the application of spintronic and magnetic sensing applications partially because of their ability to form several different metastable phases. Similarly, rare-earth nitrides have been studied for over 50 years due to their optical properties and strong electron correlations, leading to behaviors that range from insulating to metallic. This study uses molecular beam epitaxy to synthesize epitaxial thin films of different Mn-, Cr-, Ga-, and Ce-nitride phases. The electrical and magnetic properties of these films are investigated with the rocksalt MnN and CrN both showing metallic behavior, with the latter showing a magnetic transition ~280K. However, when combining these materials at similar growth conditions, instead of maintaining the rocksalt structure, a new ternary cubic phase of  $Mn_xCr_yN$  is obtained which shows narrow-gap semiconducting behavior. Additionally, density functional theory calculations show potential new phases where lanthanoid ternary phases are experimentally realizable. This work presents an avenue for the epitaxial integration of metallic, magnetic, and semiconductor materials via transition metal and lanthanoid compounds, en route to the synthesis of actinoid compounds.

5:00pm **AC+AS+MI+TH-WeA-9 Formation and Electronic Properties of Uranium Tellurides: A Thin Films Study, Evgenia Tereshina-Chitrova, S. Alex**, Institute of Physics CAS, Prague, Czechia; *O. Koloskova, L. Horak*, Charles University, Prague, Czechia; *O. Romanyuk, Z. Soban*, Institute of Physics CAS, Prague, Czechia; *T. Gouder, F. Huber*, JRC Karlsruhe, Germany

Understanding the interaction of 5f electrons with other electrons in actinide compounds presents a significant challenge. Factors such as relativistic effects, strong electron correlations, and hybridization with ligands contribute to the complexity of observed effects. This complexity is exemplified in the case of the recently discovered unconventional superconductor  $UTe_2$  [1]. The ongoing debate surrounding  $UTe_2$  revolves around understanding its unconventional superconductivity, the nature of its electronic correlations [2,3], and the character of the 5f electrons. While it's evident that  $UTe_2$  exhibits intermediate occupancy of the 5f states at ambient pressure, there are two opposing interpretations of experimental findings regarding the degree of localization of the 5f electrons: the model based on  $5f^26d^1$  states with singlet crystal field states [4,5], and a  $5f^3$ -based model with atomic Kramers doublet and greater 5f itinerancy [6,7]. Interestingly enough, ab-initio calculations considering the  $4f^2$  U-ion ground state multiplet reproduce bulk experimental observations, such as the Schottky anomaly and magnetic anisotropy at low temperatures [8].

To contribute to this subject, we provide a comprehensive and detailed investigation of thin films of uranium tellurides with various compositions  $U_xTe_y$  by means of X-ray Photoelectron Spectroscopy (XPS) and Ultra-violet Photoelectron Spectroscopy (UPS). We also explore the structural and bulk

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properties of the films, including their magnetic and transport characteristics. This comprehensive approach allows us to correlate the changes in XPS spectra across different compositions and crystal structures with resultant bulk properties, contributing to our understanding of the nature of the 5f electrons within uranium tellurides.

The work by E.A. T.-Ch. is supported by the Czech Science Foundation (GAĀr) under the grant number 22-19416S. E.A. Ch.-T. is a recipient of the L'Oreal-UNESCO for Women in Science prize.

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- [2] I. M. Hayes et al., *Science*, 373, 797 (2021).
- [3] C. Duan et al., *Phys. Rev. Lett.* 125, 237003 (2020).
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- [5] S. Liu et al., *Phys. Rev. B* 106, L241111 (2022).
- [6] S. Fujimori et al., *J. Phys. Soc. Jpn.* 88, 103701 (2019).
- [7] F. Wilhelm, *Commun. Phys.* 6, 96 (2023).
- [8] S. Khmelevsyy et al., *Phys. Rev. B* 107, 214501 (2023).

5:20pm **AC+AS+MI+TH-WeA-10 Nanoscale Uranium and Thorium Oxides for Applications in Advanced Nuclear Fuels**, *Matthew Heaney, L. Moreau, X. Guo*, Washington State University

Nanomaterials of uranium and thorium oxides and their mixtures are of significance to the development of advanced nuclear fuels with properties such as self-healing and greater fission gas retention. They also serve as a means for furthering our understanding of spent nuclear fuel behaviors. Furthermore, thorium incorporation into the uranium sublattice induces changes in oxidation behavior, which would be a promising means to provide additional redox resistance. Coupling this with the possible application in fast neutron reactors presents a potential fuel for the Th fuel cycle, which is inherently proliferation resistant. However, these possible applications are purely hypothetical given that, compared to nanomaterials from the rest of the periodic table, actinide nanomaterials are heavily understudied. Therefore, it will be imperative to interrogate the properties of these nanomaterials. This work aims to explore three key areas. (1) How careful kinetic control through variations in synthetic methods can be used to produce particles with different sizes, shapes, and heterogeneities of mixing. (2) Elucidation of the structural and thermodynamic properties of these nanomaterials and how characteristic size, shape, and heterogeneity of mixing affect them through a variety of X-ray characterization and calorimetry techniques. X-ray characterization techniques such as X-ray absorption spectroscopy (XAS) is used to evaluate the heterogeneity of mixing, local structure, and oxidation state of particles while small-angle X-ray scattering (SAXS) is used to determine statistical values on particle size, shape, and polydispersity. Calorimetry techniques like high temperature drop calorimetry are used to determine enthalpies of formation for nanoparticles and the contribution surface effects have on the thermodynamics or thermogravimetric analysis-differential scanning calorimetry (TGA-DSC), which can be used to evaluate oxidation behaviors. (3) How sintered nanoparticles behave in *in-situ* reactor conditions as nuclear fuels and how particle characteristics can be chosen to achieve more desirable radiation-resistance and thermal properties for nuclear fuel, through irradiation studies performed at the 1-MW TRIGA reactor on the campus of Washington State University. Overall, the work presented provides initial evidence for the benefits of nanomaterials in the production of advanced reactor fuels and outlines important fundamental properties of actinides on the nanoscale.

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