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Editorial: Structures and properties of fluorite-related systems for nuclear applications

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Editorial on the Research Topic

[Structures and properties of fluorite-related systems for nuclear applications](#)

1 How does an incidentally simple structure integrate such fundamental scientific complexity?

Fluorite-like materials are used in nuclear applications as advanced fuels such as MOX fuels and transmutation fuels. These materials exhibit high resistance to radiation-induced amorphization (Wiss et al., 2013; Yasuda et al., 2020). In these systems, there appear to be specific differences in the detailed response to radiation due to the competition between the spatial correlations of cations and anions describing their organization. Under irradiation, a sharp decrease in the characteristic spatial correlation length describing the O-vacancy order is usually observed. However, once the radiation is turned off, the disordered fluorite phase is suddenly quenched to a broken symmetry phase, in which domains with spatial correlations of the vacancies form and become coarser over time as the system tries to reach local equilibrium on ever larger length scales. This process of returning to equilibrium occurs while maintaining a much longer correlation length of the cation sublattice, thus preserving crystallinity over long distances, so that the system effectively behaves as a paracrystal (Tilley, 1987; Solomon et al., 2025). The properties of fluorite systems are generally explained by microanalysis and less frequently by holistic approaches. The transition from an ideal system studied in isolation to an interacting and open system is extremely difficult. Knowing the organization of the microstructures, local structures, defects and chemical substitutions in relation to their interaction with the environment is an increasingly challenging task, especially in multicomponent systems, such as those covered in this Research Topic of articles. These systems are inherently complex and much more challenging because they rarely reach true thermodynamic equilibrium below the temperature at which they chemically order (usually 1,200 K) (Sørensen, 1981; Herrero et al., 1990). Metastable configurations and harsh energy landscapes are

promoted by the low mobility of the substituted cations within the temperature range characteristic of nuclear fuel operation. Only at high temperatures can kinetic control of the defect structure be expected. For these reasons, the structural and functional properties of substituted systems remain a challenging field for experimentalists and theorists alike. These studies, therefore, often require a collaborative approach, in which a problem is investigated across different scales and disciplines. This brings challenges to the functioning of collaborations and information exchange between traditional disciplines. The success of this community reminds us that research itself is a complex system and that results are best studied by looking at them from many perspectives. Quoting Edgar Morin: “The paradigm of complexity thus stands as a bold challenge to the fragmentary and reductionistic spirit that continues to dominate the scientific enterprise”. Nuclear materials are undoubtedly a field that faces this great challenge.

2 A crosscutting research topic

The application of diffraction, microscopy and spectroscopy techniques allows researchers to understand remarkable details of polymorphic and morphotropic phase transformations in pristine samples, but also in out-of-equilibrium conditions that are typical of radiation damage. In Figure 1 a TEM bright field image and its corresponding electron diffraction shows the microstructural reorganization of a reactor irradiated UO_2 fuel. Understanding and modeling microstructural evolution and phase stability under chemical and physical conditions relevant to applications, along with chemical and structural evolution at interfaces, is of paramount importance to understanding and designing materials and material interfaces that can withstand radiation, where temperature gradients and chemical phenomena can span multiple length and time scales. These observations and models provide valuable information for the fabrication and performance of advanced nuclear fuels, especially those containing minor actinides. In these complex systems, understanding thermodynamics, transport and chemical behavior remains challenging, but it also provides opportunities for developing new approaches to nanoscale characterization and simulation. The collective contributions of these six articles provide an overview and underscore the potential of techniques and models in advancing our understanding of advanced nuclear ceramic materials with fluorite-related structures.

Burakovsky et al. at the Los Alamos National Laboratory (United States) modelled the Liquidus Curve of the Uranium-Plutonium Mixed Oxide (MOX) System, which is currently considered as a reference fuel for some of the generation IV fast breeder reactors. The key factor determining the performance and safety of fuels such as MOX depends on their operational limits in the application environment which are closely related to the material's structure and thermodynamic stability. These limits are, in turn, closely related to the ambient (zero pressure) melting point (T_m). In their study, Burakovsky et al. presented a theoretical model of the melting curve (liquidus) of an ideal mixture of pure UO_2 and PuO_2 . The model has the merit of linking liquidus points with equations of state for single oxides and mixtures, which is certainly an

original and useful approach. The model has only one free parameter, which must be determined independently. Examples of the application of the model to real mixtures, Si-Ge and MOX, considered in their work clearly demonstrate that, although the model is not based on rigorous thermodynamic arguments, it is reliable and relatively easy to apply in practice, in contrast to more complicated and more time-consuming Calphad calculations.

In a second article, Burakovsky et al. presented a Quantum Molecular Dynamics study of the higher-temperature portion of the phase diagram of the uranium-oxygen system, including the Ambient Melting Behavior of Stoichiometric Uranium Oxides. As UO_2 is easily oxidized during the nuclear fuel cycle it is important to have a detailed understanding of the structures and properties of its oxidation products. Experimental work over the years has revealed many stable uranium oxides, including UO_2 , U_4O_9 ($\text{UO}_{2.25}$), U_3O_7 ($\text{UO}_{2.33}$), U_2O_5 ($\text{UO}_{2.5}$), U_3O_8 ($\text{UO}_{2.67}$), and UO_3 , all of which have a number of different polymorphs. These oxides are broadly split into two categories: fluorite-based structures with stoichiometries in the range of UO_2 to $\text{UO}_{2.5}$ and less dense, layered-type structures with stoichiometries in the range of $\text{UO}_{2.5}$ to UO_3 . While UO_2 is well characterized experimentally and computationally there is a paucity of data in the literature concerning higher stoichiometry oxides. In their work, Burakovsky et al. determined the ambient melting points of all six stoichiometric uranium oxides listed above and compared them to available experimental and/or theoretical data. They demonstrated that the six ambient melting points form a family that maps out a solid-liquid transition boundary consistent with the high-temperature portion of the uranium-oxygen phase diagram.

Lewis et al. from the University of Bristol (UK) and co-authors assessed the Charge-Lattice Coupling and Dynamic Structure of the U-O Distribution in UO_{2+x} by examining the different structures and behaviors of UO_{2+x} observed in the crystallographic and local structures using Extended X-ray Absorption Fine Structure (EXAFS) measurements of pristine $\text{UO}_{2.0}$, or bulk U_4O_9 and U_3O_7 irradiated with protons or helium or at multiple temperatures and thin film $\text{U}_4\text{O}_{9-\delta}$ on an epitaxial substrate. The disorder caused by irradiation was observed to be mostly limited to increased widths of the existing U-O/U pair distributions with any new neighbor shells being minor. As previously reported, disorder caused by oxidative addition to U_4O_9 and U_3O_7 is much more extensive, resulting in multisite U-O distributions and a greater reduction of the U-U amplitude with different distributions in bulk and thin film U_4O_9 . In addition to indicating that these anomalies only occur in the mixed valence materials, this work confirms the continuous rearrangement of the U-O distributions from 10 to 250 K. Although these structural variations are not observed in crystallography, their prominence in the EXAFS indicates that the dynamic structure underlying these effects is an essential factor in these materials.

Gaillard et al. from the Institut de Physique des 2 Infinis (France) and co-authors also investigated the effects of non-stoichiometry and presented new insights into the study of the $\text{UO}_{2+x}/\text{U}_4\text{O}_9$ equilibrium in UO_2 as a function of hyperstoichiometry by coupling HERFD-XANES at the uranium M4-edge with micro-Raman spectroscopy mapping. While XANES allowed the measurement of uranium speciation in the samples, Raman spectroscopy was used to characterize individually the composition and localization of the different oxide phases. As the O/U increased, the authors were able to evidence the formation of a network

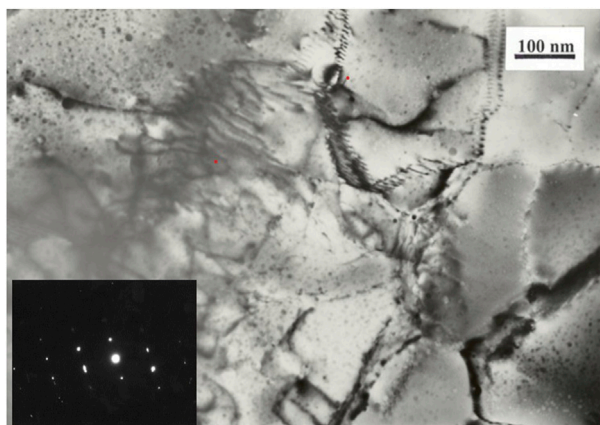


FIGURE 1
TEM bright field image of an irradiated UO_2 fuel at 75 GWd.t^{-1} showing that the harsh irradiation conditions result in microstructural reorganization with the formation of low-angle grain boundaries (in this case) and of extended defects (dislocation lines/tangles, loops) along with fission gas bubbles while the fluorite structure is kept as confirmed by electron diffraction.

of U_4O_9 that had crystallized inside UO_{2+x} grains. The variation of the UO_{2+x} phase hyperstoichiometry (x) was then evaluated as a function of the sample oxidation.

Wiss et al. of the Joint Research Centre of the European Commission and co-authors measured the heat capacity of alpha-damaged uranium, plutonium, and americium mixed dioxide ($\text{U}_w, \text{Pu}_w, \text{Am}_w$) $\text{O}_{2\pm x}$ samples during thermal annealing. The excess of heat released was assessed and the recovery stages associated with various defects were described by integrating results from transmission electron microscopy, helium desorption spectroscopy, thermal diffusivity, and XRD annealing studies. The study shows that different defect-annealing stages can be singled out. It was also evidenced that the excess of energy stored in defects tends to saturate at rather low damage levels. However, with increasing radiogenic helium production, another source of stored energy emerged, which can be attributed to the formation of He-defect complexes that cannot be annihilated until higher temperatures are reached.

Finally, Yao et al. from the Pacific Northwest National Laboratory (United States) described the development of a novel *in situ* particle-attached Microfluidic Electrochemical Cell based on a vacuum-compatible microfluidic electrochemical cell (E-cell) for investigating the redox behavior of uranium dioxide. Experiments using bulk amounts of radioactive material can be costly and require shielded hot cell facilities. In contrast, the amount of radioactive material used in a single test could be significantly reduced by using microfluidic techniques, potentially enabling electrochemical experiments to be conducted outside of a shielded facility. The different approaches for building a microfluidic E-cell are described, which all use UO_2 as the working electrode, with the ability to characterize the corroding materials *in situ*. The authors found that

embedding UO_2 particles in a polyvinylidene fluoride binder was the most effective method, and further demonstrated that particle-based electrodes could provide an effective and low-cost solution for microfluidic electrochemical applications. The *in-situ* microfluidic E-cell offers a promising method for investigating the corrosion of UO_2 and other materials while reducing the amount of materials needed for analysis to the microgram level.

TEM bright field image of an irradiated UO_2 fuel at 75 GWd.t^{-1} showing that the harsh irradiation conditions result in microstructural reorganization with the formation of low-angle grain boundaries (in this case) and of extended defects (dislocation lines/tangles, loops) along with fission gas bubbles while the fluorite structure is kept as confirmed by electron diffraction.

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