Experimental report

04/11/2019

Proposal: **5-21-1119** **Council:** 10/2018

Title: The crystal structure of U_3O_7: Refinement of oxygen positions from neutron diffraction data

Research area: Materials

This proposal is a new proposal

Main proposer: **Gregory LEINDERS**

Experimental team:
Gregory LEINDERS
Christian SCHREINEMACHERS
Gianguido BALDINOZZI

Local contacts:
Clemens RITTER
Emmanuelle SUARD

Samples:
U3O8
U4O9
U3O7

Instrument	Requested days	Allocated days	From	To
D2B	4	2	16/07/2019	18/07/2019

Abstract:

Uranium(IV) oxide (UO2) shows a tendency to oxidize when exposed to oxidizing compounds, but conversion to the thermodynamically more stable oxide U3O8 is usually undesirable because it is associated with a structure modification and volume expansion of about 36%. Oxidation of UO2 is a complex process involving long-range ordering of oxygen clusters in a fluorite-type parent structure. We focus here on the intermediate oxide U3O7, which is the last phase based on this arrangement before the transition to U3O8 occurs. Recently our group performed electron diffraction experiments on a U3O7 sample prepared at thermal equilibrium. The results allowed to unambiguously assign the symmetry involved in its long-range ordered structure. The proposed structural model, however, is different from the model derived from earlier neutron diffraction experiments which were performed in out-of-equilibrium conditions during the isothermal oxidation of a UO2 sample. Accurately collected neutron diffraction data on a set of U3O7 samples are essential to further refine the structural model, and to understand the transition to U3O8 in the oxidation process.

The crystal structure of U_3O_7: Refinement of oxygen positions from neutron diffraction data

Neutron diffraction measurements were performed on five different uranium oxide materials, during two days of beamtime at D2B (wavelength 1.594 Å). The main focus was to obtain accurate diffraction data on the closely-related compounds U_3O_7 and U_3O_8, between 1.5 K and room temperature. Therefore, these samples were measured in the standard orange cryostat. Diffraction patterns were collected between 0 – 160 °2θ. A scan of the empty cryostat was provided by the local contact, to interpret contribution to the scattered intensity, occurring mainly around 39.6, 46.3 and 151.0 °2θ.

High-quality data was collected at 1.5 K, 50 K and at room temperature. The purpose of measuring low-temperature data was twofold: (1) to obtain diffraction data with low thermal displacement factors, and (2) to assess whether any signs of magnetic ordering effects could be revealed. Additionally, the measurements were unique in the sense that no such data on both compounds was yet reported in the open literature. No indications for magnetic ordering occurring at low temperature were observed. However, it should be considered to make use of a different beamline, optimized to working with a higher flux (such as D20), to better judge on this topic.

The neutron diffraction data was evaluated using Jana2006 [1]. The data quality was excellent for the main purpose of the study, i.e. Rietveld refinement of the crystal structure (more specifically the anion atomic positions). A new structural model of the U_3O_7 phase was proposed recently from X-ray and electron diffraction measurements [2]. The structure presents a tetragonal deformation of the classical fluorite structure of UO_2, where additionally, the excess anions group into so-called cuboctahedral oxygen clusters which are arranged in a long range ordered structure. The space group of the supercell could be derived, however, the applied diffraction techniques did not allow to quantitatively assess the atomic positions. The neutron diffraction dataset obtained at D2B allowed us to more-deeply evaluate the structural model, and in particular, the positions of the anions. A comprehensive interpretation of the results is on-going, but the first assessment shows that (1) the structural model explains the observed intensities, (2) cation positions are slightly different from the earlier, "fluorite" positions, (3) anion positions are more severely affected, and the cuboctahedra appear highly distorted from the regular configuration (see Figure 1).

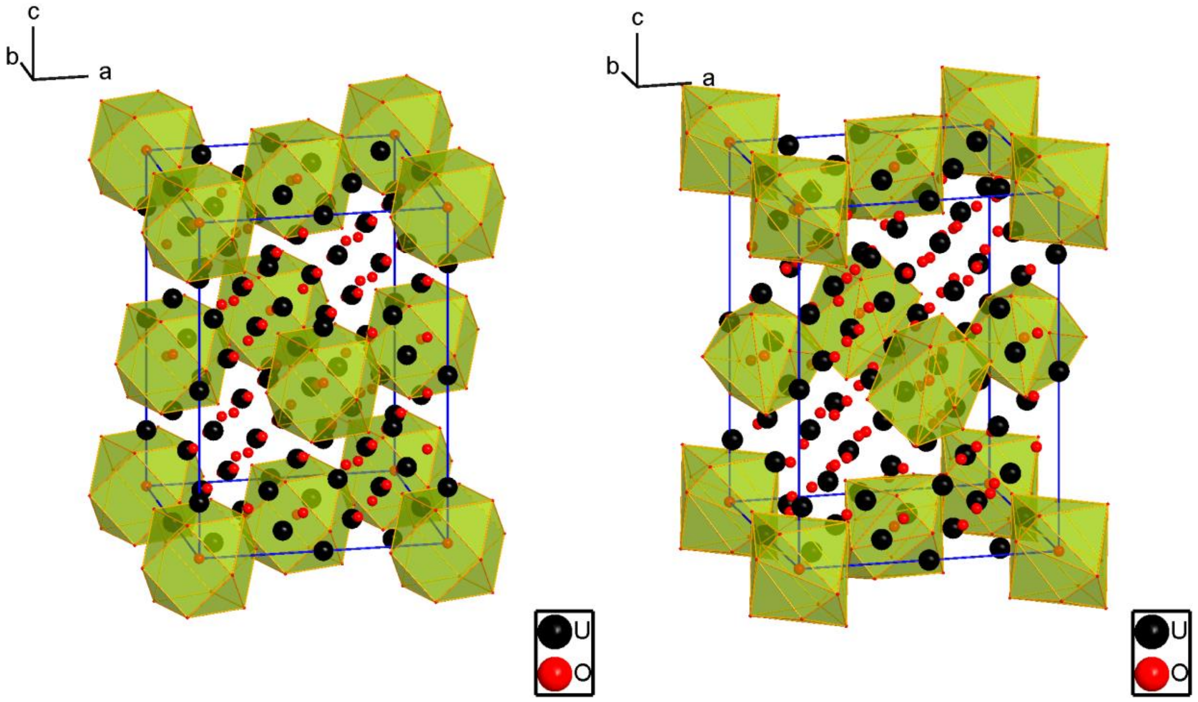

Figure 1. Superstructure model of U_3O_7, (left) proposed from X-ray and electron diffraction investigations and assuming regular oxygen cuboctahedra [2], (right) refined model based on Rietveld analysis of room temperature neutron diffraction data measured at D2B, showing displacements on the atomic positions.

To enhance our understanding of the transformation of U_3O_7 into U_3O_8, diffraction experiments were performed also on the stable end member U_3O_8, as well as on a mixture of U_3O_7 and U_3O_8 (thermally treated to promote growth of U_3O_8 from the U_3O_7 phase). Preliminary evaluation of the U_3O_8 diffraction data confirms the crystallographic information originally reported [3], but the assessment of the novel low-temperature data is still on-going. The diffraction data on the mixture sample shows that the parent reflections of the U_3O_7 phase are slightly modified owing to the partial conversion into U_3O_8, but the superstructure reflections appear unaffected. A detailed analysis is on-going.

Lastly, diffraction experiments were performed on related systems of uranium oxide, containing one lanthanide element (Nd or Ce) as dopant. Oxidation experiments have shown that, in contrast to expectations, the U_3O_8 phase is not formed, but instead a fluorite-like structure is maintained. The addition of lanthanide elements seem to stabilize this structure, of which no detailed structural information is yet available in open literature. On-going research activities at our institute showed that long-range ordering is also involved: In electron diffraction patterns sharp satellite reflections are observed in the Ce-doped sample, whereas in case of the Nd-sample a more diffuse scatter at similar positions occurs. These observations were reproduced by the neutron diffraction experiments (see Figure 2). This unique set of diffraction data present valuable information to be further evaluated, which will help to unravel the crystallographic structure of these interesting compounds.

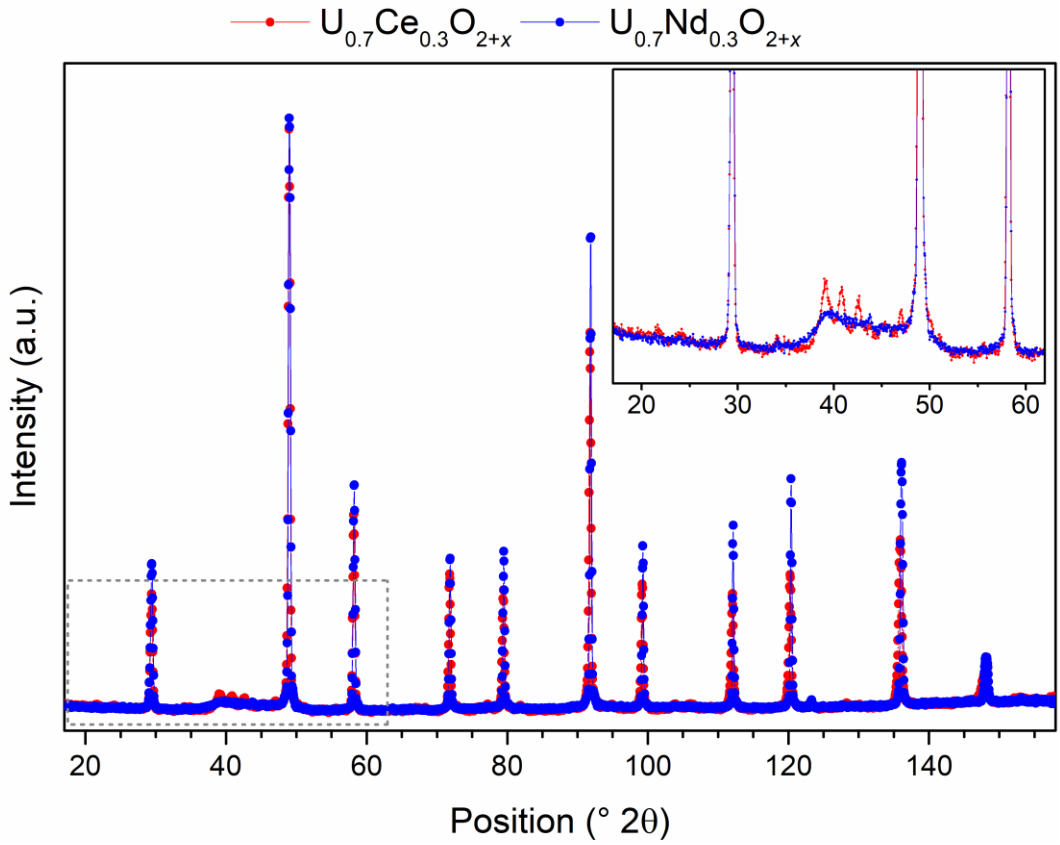

Figure 2. Neutron diffraction data measured on lanthanide-doped uranium oxide systems in a fluorite-type configuration. Superstructure reflections are observed clearly around 40 °2θ in the Ce-doped sample, whereas in this region only diffuse scatter is observed in the Nd-doped sample.

[1] V. Petříček, M. Dušek, L. Palatinus, "Crystallographic Computing System JANA2006: General features", in: Zeitschrift für Kristallographie - Crystalline Materials, 2014, pp. 345.

[2] G. Leinders, R. Delville, J. Pakarinen, T. Cardinaels, K. Binnemans, M. Verwerft, Inorg. Chem., 55 (2016) 9923.

[3] B.O. Loopstra, Journal of Inorganic & Nuclear Chemistry, 39 (1977) 1713.