Accurate lattice parameter measurements of stoichiometric uranium dioxide

Gregory Leinders [a,b,*], Thomas Cardinaels [b], Koen Binnemans [a], Marc Verwerft [b]

[a] KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium
[b] Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science, Boeretang 200, B-2400 Mol, Belgium

HIGHLIGHTS

- The lattice parameter of stoichiometric uranium dioxide has been re-evaluated.
- The new value is substantially higher than the generally accepted value.
- The new value has an improved precision.
- Earlier published values on the lattice parameter of UO_2 are carefully re-assessed.
- High accuracy was obtained on both stoichiometry and lattice parameter measurements.

ARTICLE INFO

ABSTRACT

The paper presents and discusses lattice parameter analyses of pure, stoichiometric UO_2. Attention was paid to prepare stoichiometric samples and to maintain stoichiometry throughout the analyses. The lattice parameter of $UO_{2.000\pm0.001}$ was evaluated as being 547.127 ± 0.008 pm at 20 °C, which is substantially higher than many published values for the UO_2 lattice constant and has an improved precision by about one order of magnitude. The higher value of the lattice constant is mainly attributed to the avoidance of hyperstoichiometry in the present study and to a minor extent to the use of the currently accepted Cu Kα_1 X-ray wavelength value. Many of the early studies used Cu Kα_1 wavelength values that differ from the currently accepted value, which also contributed to an underestimation of the true lattice parameter.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

UO_2 exhibits a homogeneous range of compositions near exact stoichiometry which have an effect on the lattice parameter. For details about the uranium–oxygen system, see e.g. the reviews of McEachern and Taylor, Guéneau et al., Chevalier et al., Kurepin, Labroche et al., Baichi et al. and references therein [1–8]. Given the difficulties to keep UO_2 at exact stoichiometry, precise lattice parameter determination is not straightforward. The lattice parameter has been evaluated as 547.04 ± 0.08 pm at 20 °C by Grønvold in 1955 [9]. This value has been adopted as principal reference also by the International Atomic Energy Agency (IAEA) [10]. Numerous other values have been published by researchers over the past decades (Table 1). Precise knowledge of the lattice parameter of uranium dioxide (UO_2) is important for engineering and research purposes.

When exposed to air, freshly reduced UO_2 powder will rapidly oxidize also at ambient temperatures. Bannister reviewed the low temperature oxidation of UO_2 and found that even for powders with low specific surface area (e.g. 0.5 $m^2\,g^{-1}$), O/U ratios of 2.006 can be found after 24 h of exposure [11]. For powders with a higher specific surface, the limiting amount of hyperstoichiometry can be much higher. The oxidation mechanism is chemisorption of oxygen which starts already at the boiling isotherm of oxygen, i.e. at −183 °C, followed by sub-surface oxidation which starts around −130 °C [12,13]. The sub-surface oxidation is limited to a depth of approximately 5 nm and it is invariant for temperatures up to 50 °C, the amount of oxygen absorbed being proportional to the surface area [13]. The oxidation of sintered polycrystalline UO_2 follows the same mechanisms and for pellets with high levels of open porosity, macroscopically measurable oxidation can be observed. For pellets which are sintered to densities above 95% of the theoretical density (T.D.), i.e. when all porosity is closed, the oxidation at ambient conditions is limited to the formation of a thin surface layer. Bulk oxidation is measured only at higher temperatures (>100 °C), where oxygen diffusion proceeds at a detectable rate [1,14].

* Corresponding author at: KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium. Tel.: +32 14 33 31 63.
E-mail address: gregory.leinders@sckcen.be (G. Leinders).

Upon oxidation the cubic lattice of UO_2 (Fig. 1) slightly distorts and contracts. Oxygen atoms are incorporated in the cubic-coordinated interstitial sites which are displaced in either the $\langle 1\,1\,0 \rangle$ or the $\langle 1\,1\,1 \rangle$ direction and oxygen vacancies are formed at the normal sites, with the uranium sublattice remaining undisturbed [15–17]. Willis concluded that the defects cluster together in defect clusters or complexes, with each complex containing interstitial oxygen atoms and vacant normal oxygen sites in the so-called 2:2:2 configuration [18]. The UO_2 lattice contraction is attributed to charge compensation: the excess oxygen is balanced by a valence shift of U^{4+} to $U^{5+/6+}$. The ionic radii of $U^{5+/6+}$ being smaller than that of U^{4+} and the higher specific charge result in a net lattice contraction. This effect is quite substantial and various contraction ratios have been reported, ranging from -5.5×10^{-3} pm to -15×10^{-3} pm per 0.001 amount of hyperstoichiometry [19–25].

Recent work by some of us reported a lattice parameter of $UO_{2.001}$ which was higher than the generally accepted value [27,28]. The focus of that work was on lattice contraction with doping and not specifically oriented on the pure UO_2 material. In the present work, we focus on undoped UO_2 and we pay specific attention to avoid deviations from stoichiometry.

For the experimental assessment of the lattice parameter of stoichiometric UO_2, we have prepared densely sintered polycrystalline pellets (T.D. >97%) under two different reducing atmospheres and for one of the conditions, we used two different feed powders. Precise X-ray diffraction and thermogravimetric measurements were performed and yielded a consistent set of data from which an accurate value of the lattice parameter of $UO_{2.000}$ is derived. The parameters influencing the accuracy of the lattice parameter are carefully analyzed and evaluated.

2. Experimental

2.1. Sample preparation

Three samples were prepared from two batches of depleted uranium oxide powder ($\sim UO_{2.1}$) obtained via Integrated Dry Route (IDR) synthesis and supplied by FBFC International (Dessel, Belgium). The two batches differed in impurity content, both being of nuclear grade. Chemical analysis of the starting material is shown in Section 3.1.

The samples were prepared using an identical approach. The as-received powder was compacted at 400 MPa into cylindrical pellets. A semi-automatic press (Specac Atlas 8T) was used with a compaction time of 30 s. The pressing die and punches were lubricated with a saturated solution of stearic acid in acetone. This ensured a safe operation of the press and the production of high
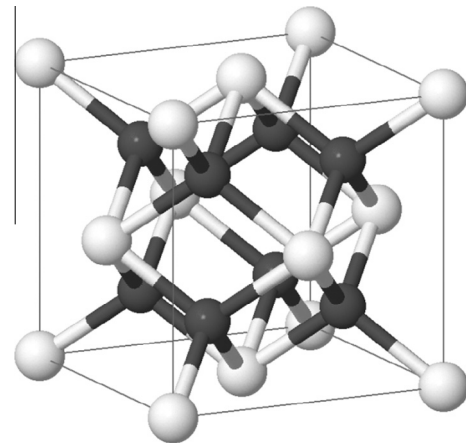

Fig. 1. Unit cell of the face-centered cubic crystal structure of UO_2. The tetrahedral-coordinated anion sites (oxygen sublattice) are shown in black. The cubic-coordinated cation sites (uranium sublattice) are shown in light gray shade. The normal interstitial sites are found in the cell edge centers (0, 0, ½), (0, ½, 0), (½, 0, 0) and the cell center (½, ½, ½). Illustration created with Jmol [26].

quality green pellets. Several UO_2 pellets were prepared for each experimental route.

Sintering was performed to reduce the $UO_{2.1}$ to stoichiometry and to densify the green bodies to almost complete density. A Linn HT 1800 Moly high-temperature furnace with an alumina matrix and molybdenum heating elements was used. The sintering atmosphere was monitored with a dew point analyzer and an oxygen analyzer. The dew point of the exiting gas is $-80\,°C$, owing to a very good gas tightness of the system. Green pellets were placed in an alumina crucible fitted with a molybdenum sheet. After placing the crucible containing the samples in the furnace, the system was sealed and flushed until the dew point of the exiting gas reached $-60\,°C$ or less.

Two different sintering conditions were used (Table 2). A heating rate of $5\,°C\,min^{-1}$ was always applied. The sintering temperature was $1680\,°C$ and maintained for 4 h. The cooling rate was inherent to the furnace and decreased logarithmic from $5\,°C\,min^{-1}$ to about $0.5\,°C\,min^{-1}$ during 15 h. Sample A was sintered under a mixture of 5 vol.% hydrogen and 0.5 vol.% oxygen in argon. Sample B and C were sintered under a gas atmosphere containing 5 vol.% hydrogen in argon. Final density was >97%, and the remaining porosity was fully closed.

2.2. Thermogravimetric analysis

The stoichiometry was measured by thermogravimetric analysis (TGA) with a Netzsch STA 449 *F1* Jupiter®. Compounds in the

Table 1
Selection[a] of the published data on the lattice parameter of UO_2.

Lattice parameter a (pm) reported	Temperature reported (°C)	Lattice parameter a (pm) at 20 °C[b]	O/U ratio stated	References
547.109 ± 0.006	25.3 ± 0.5	547.081	2.001	Cardinaels [27]
547.0[c]	20	547.0	2[d]	Hutchings [29]
546.96 ± 0.04[e]			2[e]	Alekseyev [24]
547.06 ± 0.05	25	547.03	2.001	Lynds [20]
546.9 ± 0.1			2.00[d]	Blackburn [14]
547.1 ± 0.1			2.00	
547.04 ± 0.08	20 ± 2	547.04	2.00	Grønvold [9]
546.91 ± 0.01[f]			2.000	Perio [19]
546.8 ± 0.1[f]			2.00	Herring [30]

[a] Values were selected from researchers that sufficiently specified their sample preparation methods, analysis methods and uncertainties.
[b] Lattice parameter values reported at a specific temperature are recalculated to 20 °C using the thermal linear expansion coefficient of UO_2 [31].
[c] Measured with neutron diffraction on a single crystal sample.
[d] Assumed value.
[e] Extrapolated result to O/U = 2.
[f] Original value converted from kX unit by multiplying a factor 100.2077 pm [32].