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New insights into the thermal expansion of Neptunium dioxide up to 2000 K

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Abstract

We report for the first time the thermal expansion of NpO_2 up to 2000 K and compare it to the one of UO_2 and PuO_2. Lattice parameters were measured as a function of temperature by *in situ* X-ray diffraction with neutral, reducing and oxidizing atmospheres. Data for NpO_2 under neutral and reducing conditions perfectly superpose. Up to 1550 K, thermal expansion varies linearly with increasing temperature. Above, thermal expansion presents a curvature towards higher lattice parameters. No bibliographic data were available for this temperature range for comparison. As for the thermal expansion of UO_2, we propose this curvature is certainly inferred by the formation of lattice defects in the oxygen sub-lattice. Expression of thermal expansion and coefficients of thermal expansion at given temperatures for NpO_2, are presented.

1. Introduction

Fundamental properties of actinide oxides have been investigated for decades to better predict and understand the behavior of nuclear fuels during irradiation. Among these parameters, thermal expansion is of first importance. Substantial efforts have been placed on UO_2 and PuO_2 as they both constitute the fuel for current nuclear reactors. In the next generation of reactors, it is intended to incorporate minor actinides (*i.e.* Am, Np, Cm)

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within the fuel. Consequently, a better knowledge of thermal expansion of minor actinides oxides, especially NpO_2, has gained further interest.

High-temperature X-ray diffraction (HT – XRD) is a suitable tool to study thermal properties of materials. Sudakov *et al.* [1], Fahey *et al.* [2] and Yamashita *et al.* [3] measured the evolution of the lattice parameter of stoichiometric NpO_2 from room temperature to 1273 K and Serizawa *et al.* [4] up to 1573 K. The thermal expansion of UO_2 shows a departure from the linear regime around 923 K [e.g. 5, 6, 7]. On the opposite, NpO_2 expansion varies linearly over the investigated temperature range. Thermal expansion expression, linear thermal expansion and coefficient of thermal expansion were subsequently determined, providing useful information for assessing NpO_2 thermal properties. However, thermal expansion data were limited to 1573 K.

In the present study, we report, for the first time, the thermal expansion of NpO_2 up to 2000 K. Measurements of the NpO_2 lattice parameter at high-temperature in reducing and inert atmospheres as well as, providing a comparison, the ones of UO_2 in reducing and inert atmospheres and PuO_2 in oxidizing and inert atmospheres, were obtained *in situ* by X-ray diffraction. The coefficient of thermal expansion for NpO_2 was determined. The results reveal an unexpected departure from the linear regime of the thermal expansion of NpO_2 from ca. 1673 K that may be related to the formation of lattice defects.

2. Experimental details

In situ high-temperature XRD measurements were performed with a Bragg-Brentano BRUKER D8 diffractometer combined with a heating unit and implemented in a glove-box dedicated to nuclear material handling (CEA Cadarache, France). The X-ray beam is supplied by a conventional Cu radiation tube source (40 kV, 40 mA). A Ni foil filters the Kβ radiations. The signal is detected by a LynX'Eye fast counting detector. The aperture of divergence and antiscattering slits is fixed at 0.3°.

In situ measurements were performed under various scanning atmospheres: pure He, He – 5%H_2 gas mixture, achievable thanks to a sealed chamber surrounding the sample holder.

About 20 mg of sample powder was spread in a thin layer on the Mo heating strip. Heating was completed by a Ta omega-shaped radiant element around the sample. A temperature calibration curve was built before any measurement campaign according to the thermal expansion of W (Wang & Reeber, 1998) acquired over the temperature range of interest, 293 – 2000 K. Taking into account the propagation of errors on the unit cell parameter measurements and the slight discrepancies in reproducibility, uncertainties on temperature are assumed to be ± 15 K.

Alignment of the goniometer setup (X-ray tube, sample holder and detector) was carried out prior to each set of measurements. Diffraction pattern were acquired over a 2θ interval from 20° to 145° by steps of 0.02° during 0.3 s, guaranteeing a good signal to noise ratio and enabling high-quality data refinements. These routine conditions lead to achieve a complete pattern in ca. 20 min.

NpO_2 sample was first heated up to 1573 K prior to measurement in a He – 5% H_2 gas mixture to ensure stoichiometry, get rid of potential impurities and of aging effects. Then, series of XRD patterns were isothermally collected from ambient temperature to 2000 K, each 50 K, and with a heating rate of 5 K/s. The lattice parameter a_0 of NpO_2 (space group *fm-3m*) at room temperature of 5.434(1) Å is in excellent agreement with the reported bibliographic data for stoichiometric specimens [2, 3, 4, 8].

Patterns were analyzed using TOPAS v.4 software package according to the Pawley method and based on the fundamental parameters approach for peak profile and pattern background. Data fits were performed considering 0 error corrections. Refinements were obtained with Rwp factors ranging from 6 to 10.

3. Results

3.1. Evolution of NpO₂ lattice parameter with temperature

Figure 1 displays the variation of the unit-cell parameter of NpO_2 from room temperature to 2000 K obtained under He and He - 5% H_2 atmospheres. Data under these two conditions perfectly superimpose, proving that NpO_2 remains stoichiometric at high temperature under a slightly reducing atmosphere. This also shows the good reproducibility of the current X-ray diffraction measurements. No phase transitions were observed within the considered temperature range.
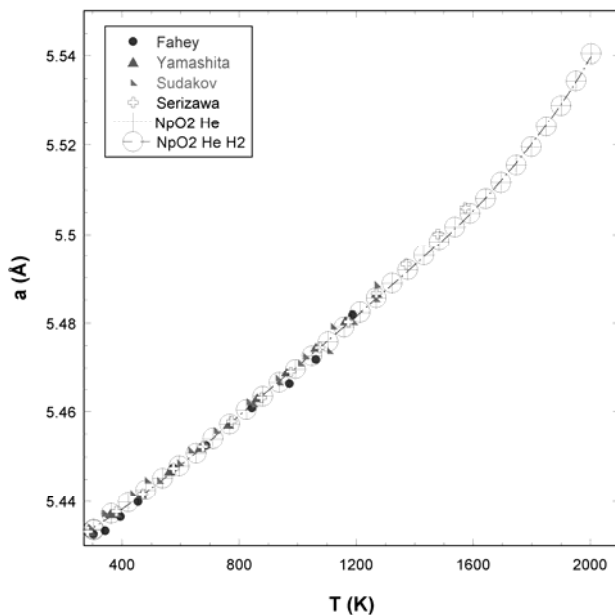

Fig. 1. Evolution of the lattice parameter a of NpO_2 as a function of temperature under He and He – 5% H_2 obtained in the present study as well as Fahey 1974; Yamashita 1997; Sudakov 1973 and Serizawa 2001. Fits of thermal expansion data for 293 K < T < 1643 K and for 1643 K < T < 2003 K to a third order expression are joined for both data set with He and He-H_2 atmospheres. Error bars for the present reported data are less than the point marks.

Available data so far were also reported as a comparison [1, 2, 3, 4]. Up to 1573 K, thermal expansion is in fairly good agreement and varies linearly with increasing temperature. At ca. 1573 K, the present high-temperature thermal expansion highlights a curvature and lattice parameters increase faster beyond 1643 K. The presence of a two-regime expansion for NpO_2 was never reported in earlier studies, However, such a behavior was observed for stoichiometric UO_2 [5, 6, 9]. At ca. 923 K, thermal expansion of UO_2 presents a change in curvature; this is usually interpreted in terms of a thermally activated formation of crystallographic defects such as Frenkel disorder in the oxygen sub-lattice [e.g. 5, 7, 10]. These defects are formed regardless of the oxidation-reduction conditions, which is in agreement with our results on NpO_2. Moreover, hypostoichiometric neptunium dioxide has only been observed at high temperature for more reduced atmosphere than in the present study, as with pure H_2 or a mixture of H_2O/H_2 ratio as of 10^{-2} [8, 11].

Thermal expansion data were adjusted according to a third order polynomial for low-temperature (293 < T < 1643 K) and high-temperature (1643 < T < 2003 K) regimes. Results are given in table 1 and fits in Figure 1.

Table 1. Expansion as a (Å) = a0 + a1 T + a2 T2 + a3 T3 for NpO_2 under He and He-H_2 atmospheres and for low-, below 1643 K (LT) and high-, above 1643 K (HT) temperature regimes.

	a_0	$a_1 \times 10^{-5}$	$a_2 \times 10^{-8}$	$a_3 \times 10^{-12}$
NpO_2 He (LT)	5.421	3.888	1.214	-2.201
NpO_2 He-H_2 (LT)	5.421	3.876	1.228	-2.254
NpO_2 He (HT)	5.386	19.54	-14.02	40.51
NpO_2 He-H_2 (HT)	5.387	19.18	-13.71	39.77

3.2. Comparison with others actinide oxides

Lattice parameters of UO_2, PuO_2 and NpO_2 are plotted against temperature in Figure 2. NpO_2 data acquired in He and He – H_2 atmospheres were brought together for clarity, owing to their reproducibility. PuO_2 and UO_2 expansion data were obtained in the same recording conditions as for NpO_2, respectively in air and He, He-H_2 gas mixture to prevent reduction or oxidation at high temperature in both cases [e.g. 7, 12]. PuO_2 lattice parameters were also obtained in He atmosphere to observe the effect of reduction on the thermal dilatation curve [12]. At low temperatures, below 1643 K, thermal expansions of those actinides display a similar quasi-linear trend. On the other hand, their high-temperature behaviors differ: at ca. 1700 K, a break occurring in the expansion curve of PuO_2 clearly indicates the reduction of the compound in He atmosphere in contrast to the preservation of stoichiometry during the oxidizing condition experiment; the curvature usually reported for stoichiometric UO_2 expansion at 1000 K [5, 7] is observed here from ca. 1600 K in reduced or neutral atmospheres. These observations show that NpO_2 seems to behave as UO_2 at high temperature in the same neutral and reducing conditions.
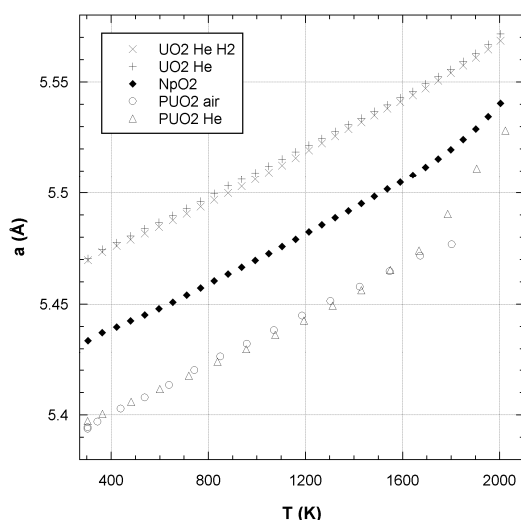

Fig. 2. Comparative thermal expansions of UO_2, NpO_2 and PuO_2 at various neutral, reduced and oxidizing conditions. NpO_2 data acquired in He and He-H_2 atmospheres were brought together for clarity.

3.3. Linear thermal expansion and coefficient of linear thermal expansion

Linear thermal expansion (l.t.e.) is obtained for NpO_2, UO_2 and PuO_2 according to the classical relation:

$$l.t.e. (\%) = (a_T - a_{293}) \times 100 / a_{293}$$

where a_T and a_{293} are the lattice parameters of the actinide dioxides at a given temperature T and at 293 K, respectively. The l.t.e. is a convenient tool to compare the thermal behaviors between actinides. A polynomial approximation for NpO_2, UO_2 and PuO_2 is available in Table 2. Until ca. 1650 K, the l.t.e. of NpO_2 is lower than that of UO_2 as already observed by Serizawa [4].

Table 2. Comparison of the polynomial expression of the l.t.e. as l.t.e. $= b_0 + b_1 T + b_2 T^2 + b_3 T^3 + b_4 T^4 + b_5 T^5$, between stoichiometric NpO_2, UO_2 and PuO_2

	b_0	$b_1 \times 10^{-3}$	$b_2 \times 10^{-6}$	$b_3 \times 10^{-9}$	$b_4 \times 10^{-12}$	$b_5 \times 10^{-16}$
NpO_2	-0.3594	1.612	-2.079	2.658	-1.473	3.032
UO_2	-0.2687	0.8731	0.06485	0.006327	-	-
PuO_2	-0.3026	0.9745	0.1263	0.05639	-	-

The coefficients of l.t.e. α_T obtained for NpO_2 and for a given temperature T as:

$$\alpha_T = 1 / a_{293} \times (\partial a_T / \partial T)$$

are summarized and compared with that from the literature for T = 293; 1200 and 1800 K in table 3. Given the shape of the thermal expansion progress, they obviously increase with temperature. At 293 K, the value of $\alpha_{293} = 8.66 \times 10^{-6}$ K^{-1} is in very good agreement with other available data. Although we obtain a slightly higher α at 1200 K than in the literature, we believe our result is more robust as this point is well controlled by high temperature measurements above 1200 K contrary to the bibliographic ones that stop at 1200 K.

Table 3. Coefficients of l.t.e. (10^{-6} K^{-1}) of NpO2 for discrete values of temperature obtained in this study and available in the literature for comparison [2, 3, 13, 14].

T (K)	293	1200	1800
this work	**8.66**	**12.5**	**15.54**
Yamashita *et al.* [2]	8.78	10.8	
Fahey *et al.* [3]	8.93*	10.9*	
Marples [13]	9.0		
Taylor [14]	8.6	11.14	

* at 298 and 1173 K respectively

4. Conclusions

We have shown in the present in situ XRD study that NpO2 certainly present lattice defects above 1550 K. It is known, at least of UO_2 [7] that these defects contribute to heat capacities Cp and mark the Cp curve by an important increase. No Cp measurements at enough high temperatures have been performed on NpO_2 to date. Further drop calorimetry and differential scanning calorimetric measurements will allow us to check the later assumption.

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