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Thermal expansions of NpO_2 and some other actinide dioxides

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Abstract

Thermal expansions of the stoichiometric actinide dioxides (ThO_2, UO_2, NpO_2 and PuO_2) were investigated between room temperature and 1300 K using a high temperature X-ray diffraction method. The lattice parameter of NpO_2 at high temperatures was expressed as a_T (pm) $= 542.03 + 4.28 \times 10^{-3}T + 9.07 \times 10^{-7}T^2 - 1.36 \times 10^{-10}T^3$. Based on excellent reproducible data, thermal expansion of NpO_2 was determined. Thermal expansions of the other actinide dioxides showed good agreement with the respective recommended literature values. The linear thermal expansion coefficients (α) of actinide dioxides calculated at 1200 K were in inverse relation to their melting points. At room temperature, however, the α value of UO_2 was found to be higher than those of the other actinide dioxides and this result was discussed.

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1. Introduction

Because of their technical importance, thermal expansions of ThO_2, UO_2 and PuO_2 were intensively studied using various techniques. These data were compiled and assessed by Thermochemical Properties Research Center (TPRC), Purdue University [1]. They presented the recommended equations of the linear thermal expansion for ThO_2 and PuO_2 and the provisional equation for UO_2. Taylor [2], also, compiled and analyzed thermal expansion data and presented regression equations of lattice parameter as a function of temperature for these actinide dioxides. For NpO_2, on the other hand, only a few data were available and these were obtained using the X-ray diffraction technique [3–5]. Marples [3] measured the lattice parameter of NpO_2 between 4 K and room temperature to investigate the change of lattice parameter near the Néel temperature (T_N) about 30 K. He found a sharp break at T_N in the lattice parameter-temperature curve. Sudakov et al. [4] and Fahey et al. [5] measured lattice parameter of NpO_2 from room temperature to about 1300 K using the high temperature X-ray diffraction technique. Measured lattice parameters were scattered considerably and the agreement between these data sets was not good: the largest difference in lattice parameters was about one picometer.

As for the linear thermal expansion coefficient (α) of actinide dioxides, Fahey et al. [5] first made comparison of their measured values and literature ones at room temperature (298 K) and at high temperature (1173 K). They found that at room temperature the α values were almost the same values of about 8.5×10^{-6} K^{-1}, but at high temperatures the α values increased with increasing atomic numbers from 10.2×10^{-6} K^{-1} for ThO_2 to 13.2×10^{-6} K^{-1} for BkO_2. On the other hand, Marples [3] noted from his low temperature experiments of these dioxides that the α values of UO_2 and NpO_2 at room temperature were somewhat higher than those of ThO_2 and PuO_2 because both UO_2 and NpO_2 had a magnetic transition.

In the present study, thermal expansions of NpO_2 as well as ThO_2, UO_2 and PuO_2 were measured using a high-temperature X-ray diffraction technique. Temperature dependence of lattice parameters and the linear thermal expansion of these actinide dioxides were compared with those of TPRC, Taylor and individual study. The linear thermal expansion coefficients of these actinide dioxides were discussed in relation to their melting points.

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2. Experimental details

2.1. Materials

Thorium dioxide microspheres were prepared from $Th(NO_3)_4$ solution using a sol-gel process followed by firing the gelled particles at 1573 K in air. Details of the process was described elsewhere [6]. The main impurities in the microsphere were Al, Fe, Mo, Si, V and Zn, and each of them was less than 10 ppm by ICP analysis.

Uranium dioxide was prepared by reducing U_3O_8 in a stream of purified hydrogen gas at 1273 K for 10 h. The U_3O_8 was prepared by oxidizing high purity uranium metal blocks with metallic impurities of less than 20 ppm [7] in air at about 1000 K.

Neptunium dioxide was provided from Fontenay auch Roses, France. The main impurities were Na (50 ppm), Si (50 ppm) and Fe (200 ppm). The isotopic purity of the ^{237}Np was higher than 99.99% by mass spectroscopic analysis.

Stocked plutonium nitrate solution was purified with an anion exchange resin (Dowex 1-X4). Plutonium oxalate was precipitated with oxalic acid from the solution and then heated in air at about 1200 K to decompose the oxalate to PuO_2. The isotopic composition was 91.63% for ^{239}Pu, 7.91% for ^{240}Pu, 0.384% for ^{241}Pu and 0.073% for ^{242}Pu by mass spectroscopic analysis.

ThO_2, NpO_2 and PuO_2 were heated in air at 1273 K and UO_2 was heated in H_2 at 1273 K before use.

2.2. X-ray diffraction study

The high temperature X-ray diffraction study was carried out using a Rigaku RAD-3C diffractometer system attached a Rigaku furnace unit. An NaI(Tl) scintillation counter in conjunction with a curved pyrolitic graphite monochromator was used to detect the Cu Kα radiation. Powder specimens were loaded on a small dent (5 mm × 5 mm) of a platinum sample holder without binder and mounted in the furnace attachment. The vacuum housing and Pt heating elements allowed examination in controlled atmospheres (He–8 vol.% H_2 for UO_2 and NpO_2 or air for ThO_2, NpO_2 and PuO_2) at high temperatures in order to have the specimen at the stoichiometric composition.

Furnace temperature was measured by an R-type (Pt/Pt13%Rh) thermocouple inserted into a thin hole of a sample holder and was controlled by a PID type temperature controller within ± 1 K during X-ray measurements. Sample temperature was determined by the lattice parameter of the Pt sample holder and the thermal expansion data of platinum [8]. A linear relation was obtained between the furnace temperature and the sample temperature. An estimated error in temperature was ± 10 K, most of which came from uncertainties in determination of the lattice parameter of platinum.

In order to recover lattice distortions in crystallites caused by self-radiation damage, each specimen was at first heated at 1273 K for 3 h in a given atmosphere, before X-ray measurement was made. Then furnace temperature was lowered by 50 K or 100 K and kept at that temperature for an hour, and then X-ray measurement was carried out. This procedure was repeated down to room temperature. The peak positions of X-ray diffraction taken at room temperature before and after heating were almost identical for ThO_2, UO_2 and NpO_2. For PuO_2, however, diffraction peaks after heating were shifted to higher angles compared to those of before heating, which suggested that the lattice was shrunk due to annealing of the self-radiation damage.

Lattice parameters were calculated from all reflections ($25° < 2\theta < 150°$) employing the least-squares method for a Nelson-Riley extrapolation. The estimated standard errors of the calculated lattice parameters were ± 0.01 pm for UO_2, NpO_2 and PuO_2 and ± 0.04 pm for ThO_2. The greater standard error for ThO_2 was attributed to poor resolutions of peaks from ThO_2 and a platinum sample holder, especially for $2\theta > 100°$, where several reflections from a platinum sample holder accidentally overlapped those from ThO_2 at elevated temperatures.

3. Results and discussion

Lattice parameters of NpO_2 are plotted against temperature in Fig. 1 and those of ThO_2, UO_2 and PuO_2 in Fig. 2. Measured lattice parameters were fitted as a function of temperature in the form of $a_T\ (\mathrm{pm}) = b_0 + b_1 T + b_2 T^2 + b_3 T^3$ where a_T is the lattice parameter at temperature T(K). The regression results and a_{293} are listed in Table 1.

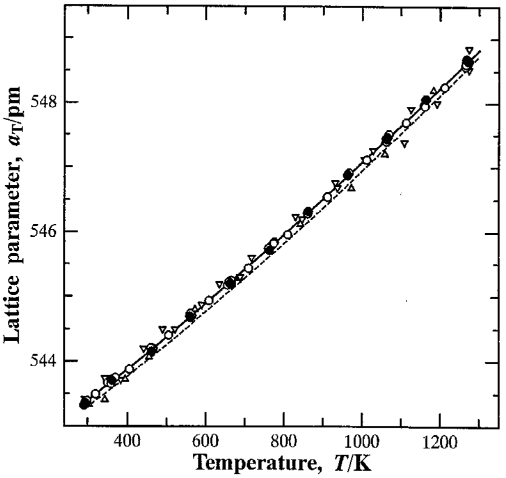

Fig. 1. Thermal expansion of NpO_2 plotted as lattice parameter versus temperature. ●: this work in He–8 vol.% H_2; ○: this work in air; △: Fahey et al. [5]; ▽: Sudakov et al. [4]. Solid and broken lines indicate the calculated values using the regression equation obtained by this work and by Taylor [2], respectively.

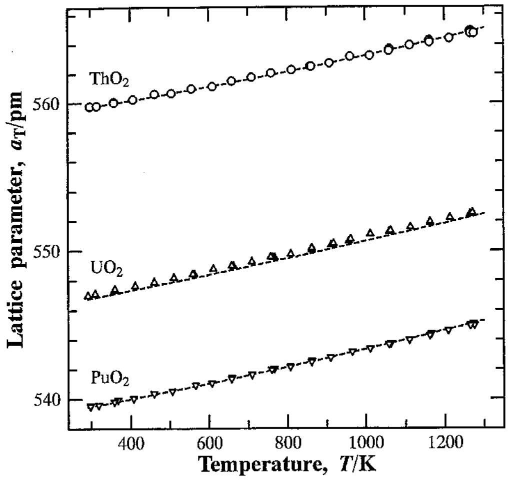

Fig. 2. Thermal expansion of ThO_2, UO_2 and PuO_2 plotted as lattice parameter versus temperature. ○: ThO_2; △: UO_2; ▽: PuO_2. Broken lines indicate the calculated values using the regression equation obtained by Taylor [2].

The estimated standard deviations are shown in the last column.

3.1. Lattice parameter at room temperature

Table 2 summarizes the typical lattice parameters of these dioxides obtained at room temperature. Present values were calculated at 298 K using the regression data listed in Table 1. It can be seen that the present values are in good line with the literature values taking the experimental errors into account.

Taylor [2] selected the value of 546.80 pm for the lattice parameter of UO_2 at 298 K and performed his regression analysis. This value for the lattice parameter of UO_2 at 298 K is apparently low compared to those obtained in the present study (547.02 pm) at 298 K and reported in the other literatures (547.04–547.05 pm) at 293–298 K. It is well known that the lattice parameter (a) of nonstoichiometric UO_{2+x} diminishes with increasing excess oxygen content (x) and that the relation between a and x at room temperature is given as

$$a\,(\mathrm{pm}) = 547.05 - 9.4x$$

by Nickel [13]. The value of 546.82 pm was also reported by Swanson and Fuyat for $UO_{2.03}$ at 299 K [14].

Table 1
Regression data for ThO_2, UO_2, NpO_2 and PuO_2. $a_T\,(\mathrm{pm}) = b_0 + b_1T + b_2T^2 + b_3T^3$

Material	b_0 (pm)	$b_1 \times 10^3$	$b_2 \times 10^7$	$b_3 \times 10^{10}$	a_{293} (pm)	ESD
ThO_2	558.348	4.628	0.4708	2.512	559.71	0.063
UO_2	545.567	4.581	10.355	−2.736	546.99	0.041
NpO_2	542.032	4.276	9.075	−1.362	543.36	0.028
PuO_2	538.147	4.452	7.184	0.1995	539.51	0.037

Table 2
Lattice parameters a of ThO_2, UO_2, NpO_2 and PuO_2 at room temperature

Material	a (pm)	T (K)	Ref.
ThO_2	559.7		[9]
	559.74	298	[2]
	559.68 ± 0.01	293	[3]
	559.72 ± 0.05	298	[10]
	559.74 ± 0.06	298	present work
UO_2	547.04 ± 0.01	298	[11]
	547.04 ± 0.08	293	[12]
	546.80	298	[2]
	547.05 ± 0.01	294	[3]
	547.02 ± 0.04	298	present work
NpO_2	543.28 ± 0.2	298	[5]
	543.33	298	[2]
	543.36 ± 0.01	296	[3]
	543.38 ± 0.03	298	present work
PuO_2	539.60 ± 0.03		[9]
	539.55	298	[2]
	539.60 ± 0.01	292	[3]
	539.54 ± 0.04	298	present work

3.2. Lattice parameter at elevated temperature

Lattice parameters of NpO_2 at elevated temperatures were measured both in air and in He–8 vol.% H_2. These are plotted in Fig. 1 together with literature values. As seen from the figure, lattice parameters measured in air (open circles) agree very closely with those measured in He–8 vol.% H_2 (filled circles), indicating that NpO_2 is the stoichiometric compound and the reproducibility of X-ray measurements was excellent. The solid line in the figure is the regression curve of the present data and the broken line is the curve calculated using data reported by Taylor [2]. Taylor's values are about 0.1 pm lower than the present values. This discrepancy may result from the fact that he made the regression calculation using the data reported by Fahey et al. [5] which are somewhat lower than the present values.

Lattice parameters of ThO_2(○) and PuO_2(▽) are in good accordance with Taylor's results which are shown by broken lines in Fig. 2. For UO_2, however, significant (beyond experimental errors) and nearly constant difference is seen between the present values (△) and those of Taylor. This difference may be caused by the smaller value which Taylor selected as the reference lattice parameter at 298 K as discussed earlier.

3.3. Linear thermal expansion

Values of linear thermal expansion (LTE) at temperature T were calculated by the relation

$$\mathrm{LTE}(T)\ (\%) = (a_T - a_0) \times 100/a_0,$$

where a_T was the lattice parameter at temperature T and

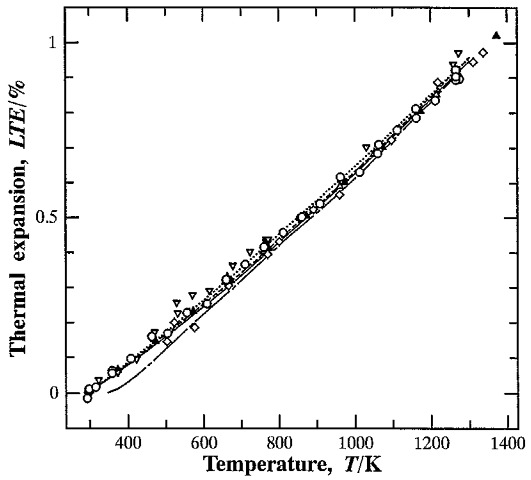

Fig. 3. Percent linear thermal expansion (LTE) of ThO_2 plotted against temperature. ○: this work; △: Kempter and Elliott [15]; ▲: Lang and Knudsen [16]; ▽: Roth and Halteman [17]; ◇: Baldock et al. [18]. Solid line is taken from TPRC [1], broken line from Taylor [2], dotted line from Wachtmann et al. [19], and dash and dotted line from Brett and Russell [20].

a_0 was that at the reference temperature 293 K. The a_0 values are listed in Table 1. Calculated results are plotted against temperature in Fig. 3 for ThO_2, in Fig. 4 for UO_2, in Fig. 5 for NpO_2 and in Fig. 6 for PuO_2, respectively. In Figs. 3–6 typical literature values of the linear thermal expansion, $(a_T - a_0) \times 100/a_0$ for lattice parameter measurements (open marks and broken lines) and $(\ell_T - \ell_0) \times 100/\ell_0$ for dilatometric measurements (closed marks and the other lines except broken lines) are also shown for comparison. Excellent agreements can be seen between the present results (open circles) and the recommended values of TPRC and Taylor which are indicated by solid and broken lines, respectively.

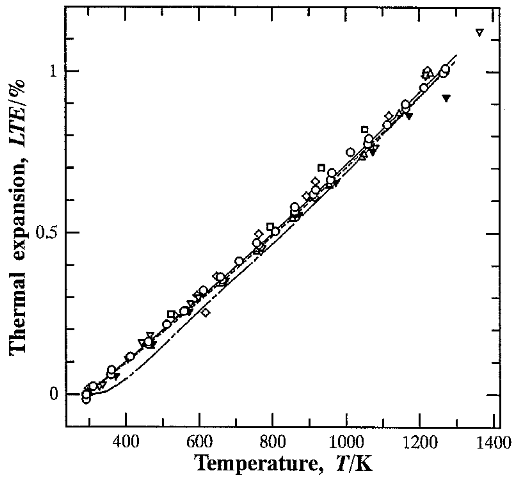

Fig. 4. Percent linear thermal expansion (LTE) of UO_2 plotted against temperature. ○: this work; ◇: Baldock et al. [11]; △: Kempter and Elliott [15]; □: Grønvold [12]; ▽: Roth and Halteman [17]; ▼: Lambertson and Handwerk [21]. Solid line is taken from TPRC [1], broken line from Taylor [2], and dash and dotted line from Brett and Russell [20].

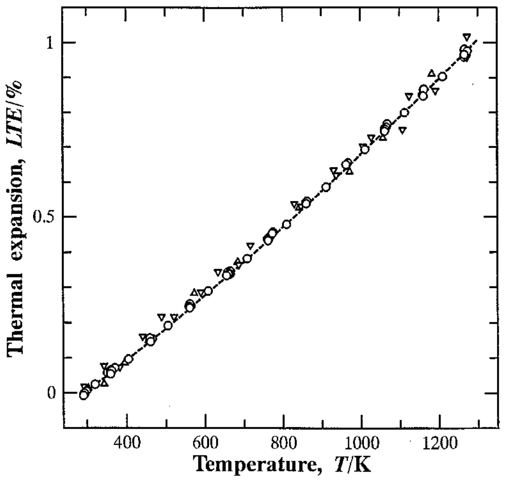

Fig. 5. Percent linear thermal expansion (LTE) of NpO_2 plotted against temperature. ○: this work; △: Fahey et al. [5]; ▽: Sudakov et al. [4]. Broken line is taken from Taylor [2].

In Figs. 7–10, deviations of linear thermal expansion (DLTE) from the present regression data are plotted against temperature to inspect differences between the present and literature data in more detail. The DLTE at temperature T was calculated with the relation

$$\mathrm{DLTE}(T)\ (\%) = \mathrm{LTE}(T)_{\mathrm{obs}} - \mathrm{LTE}(T)_{\mathrm{ref}},$$

where $\mathrm{LTE}(T)_{\mathrm{obs}}$ was the measured value and $\mathrm{LTE}(T)_{\mathrm{ref}}$ was the calculated value using the present regression data.

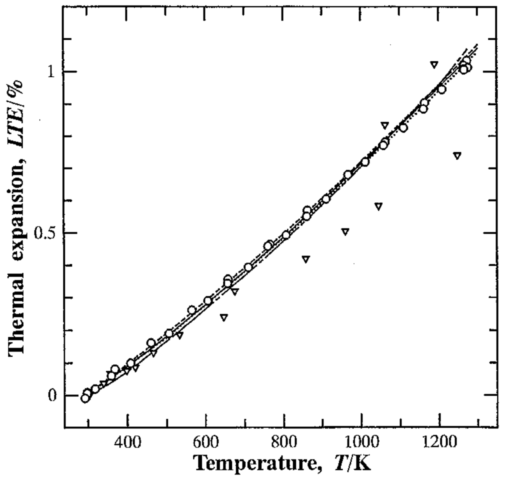

Fig. 6. Percent linear thermal expansion (LTE) of PuO_2 plotted against temperature. ○: this work; ▽: Roth and Halteman [17]. Solid line is taken from TPRC [1], broken line from Taylor [2], dotted line from Tokar et al. [22], and dash and dotted line from Brett and Russell [20].

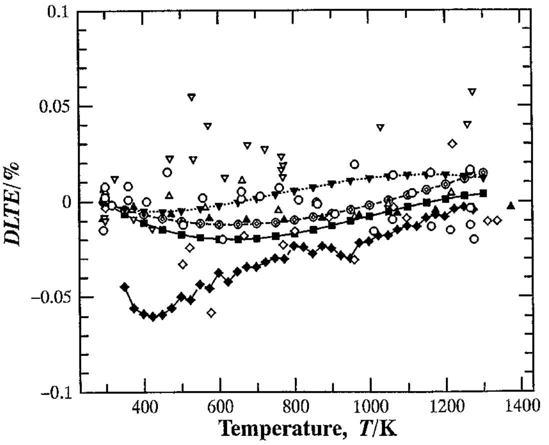

Fig. 7. Deviation of percent linear thermal expansion (DLTE) of ThO_2 plotted against temperature. ○: this work; ■: TPRC [1]; ⊚: Taylor [2]; △: Kempter and Elliott [15]; ▲: Lang and Knudsen [16]; ▽: Roth and Halteman [17]; ◇: Baldock et al. [18]; ▼: Wachtmann et al. [19]; ◆: Brett and Russell [20].

In these figures, open marks indicate these data obtained by high temperature X-ray diffraction study and filled marks indicate the data obtained with either dilatometric or interferometric methods.

For ThO_2 as shown in Fig. 7, measured points of the present study are distributed within ±0.02%. DLTE of TPRC [1], Taylor [2], Wachtmann et al. [19] and Lang and Knudsen [16] lie also within ±0.02%. However, it is found that values of TPRC and Taylor deviate slightly in the negative way below 1000 K and those of Wachtmann et al. in the positive way above 600 K.

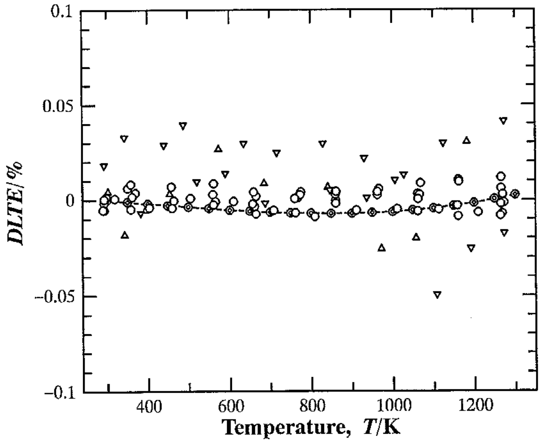

Fig. 9. Deviation of percent linear thermal expansion (DLTE) of NpO_2 plotted against temperature. ○: this work; ⊚: Taylor [2]; ▽: Sudakov et al. [4]; △: Fahey et al. [5].

Fig. 8 shows the DLTE-temperature curves for UO_2. The present measured points are distributed within ±0.02%. DLTE of TPRC and Taylor lie also within ±0.02%. It can be seen from the figure that those of Taylor deviate negatively in the temperature range below 1300 K. Though data of TPRC are in excellent agreement with the present data below 1000 K, they deviate positively with a high slope above 1000 K. As seen in Fig. 8, data obtained by the earlier X-ray diffraction studies scatter considerably [11,12,17].

Fig. 9 shows the DLTE-temperature curves for NpO_2. The present measured points are distributed within ±0.01%. An excellent agreement can be seen between the present data and those of Taylor.

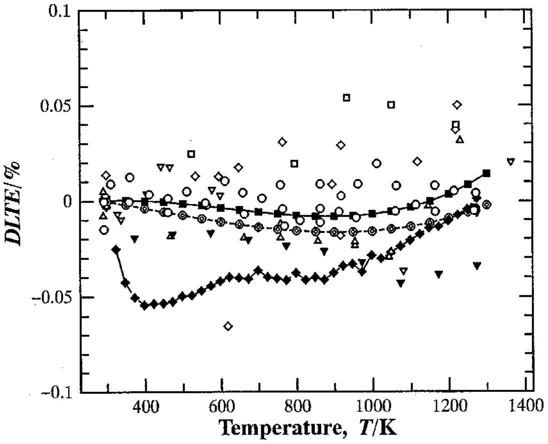

Fig. 8. Deviation of percent linear thermal expansion (DLTE) of UO_2 plotted against temperature. ○: this work; ■: TPRC [1]; ⊚: Taylor [2]; ◇: Baldock et al. [11]; □: Grønvold [12]; △: Kempter and Elliott [15]; ▽: Roth and Halteman [17]; ◆: Brett and Russell [20]; ▼: Lambertson and Handwerk [21].

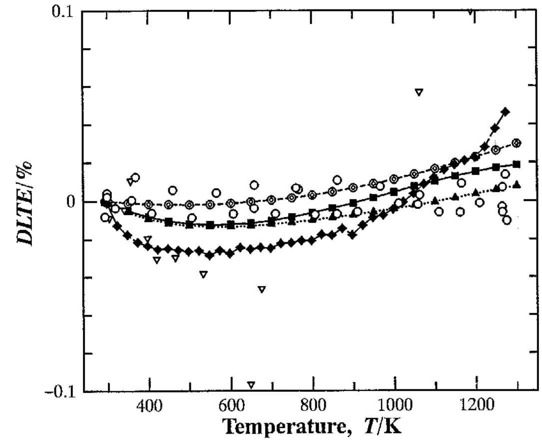

Fig. 10. Deviation of percent linear thermal expansion (DLTE) of PuO_2 plotted against temperature. ○: this work; ■: TPRC [1]; ⊚: Taylor [2]; ▽: Roth and Halteman [17]; ◆: Brett and Russell [20]; ▲: Tokar et al. [22].

In Fig. 10, the DLTE-temperature curves for PuO_2 are shown. The present measured points are distributed within ±0.02%. DLTE of TPRC and Tokar et al. [22] lie also within ±0.02%. Though data of Taylor are in excellent agreement with the present data below 800 K, they deviate positively to about 0.03% at 1300 K.

3.4. Linear thermal expansion coefficient

Linear thermal expansion coefficient α_T can be calculated by differentiating the expansion curve a_T with temperature T:

$$\alpha_T = \frac{1}{a_{293}}\left(\frac{\partial a_T}{\partial T}\right),$$

where a_{293} is the lattice parameter at 293 K. α_T values calculated at 293 and 1200 K are listed in Table 3, together with the literature values. The melting points (T_m) of actinide dioxides are also listed in the last row in the table.

These α values at 293 and 1200 K are plotted against $1/T_m$ in Fig. 11. It is generally known that the α_T values decrease in inverse proportion to the T_m values [23]. At 1200 K, a good linearity can be seen between the present α values and $1/T_m$. At room temperature, the α value of UO_2 is apparently higher than the rest which lie on a straight line. Fahey et al. [5] reported that at room temperature the α values of actinide dioxides were almost the same value of about 8.5×10^{-6} K^{-1}. On the other hand, Marples [3] pointed out that the α values of UO_2 and NpO_2 were higher than those of ThO_2 and PuO_2 at room temperature. He ascribed the high α values of UO_2 and NpO_2 to their magnetic transitions occurring at about 30 K. In this study, the α value of NpO_2 at room temperature lies between the α values of ThO_2 and PuO_2. Therefore, another possibility for an anomalously high α value of UO_2 may come from its low Debye temperature; 182 K for UO_2, 347 K for ThO_2 and 348 K for PuO_2.

Table 3
Linear thermal expansion coefficients at 293 and 1200 K for the actinide dioxides

	ThO_2	UO_2	NpO_2	PuO_2
At 293 K ($\times 10^{-6}$)				
This work	8.43	9.36	8.78	9.04
Marples [3]	7.3 [a]	9.3 [a]	9.0 [a]	8.4 [a]
Fahey et al. [5]	8.21	8.71	8.92	8.71
Taylor [2]	7.76	9.01	8.60	8.84
TPRC [1]	7.7	9.4	–	8.1
At 1200 K ($\times 10^{-6}$)				
This work	10.41	10.76	10.80	11.61
Fahey et al. [5]	10.24	12.35	10.99	12.14
Taylor [2]	11.00	11.31	11.14	12.27
TPRC [1]	10.4	11.6	–	12.0
Melting point (K)	3493	3113	2833	2663

[a] Those values were obtained at 300 K and not shown in Fig. 11.

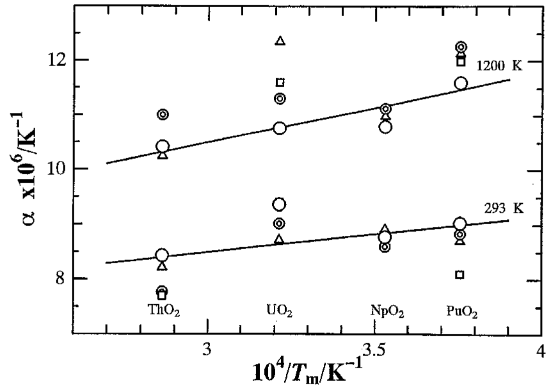

Fig. 11. A comparison of linear thermal expansion coefficients for actinide dioxides as a function of their inverse melting temperatures. ○: this work; □: TPRC [1]; ⊚: Taylor [2]; △: Fahey et al. [5].

4. Conclusions

Thermal expansions of the stoichiometric actinide dioxides (ThO_2, UO_2, NpO_2 and PuO_2) were investigated between room temperature and 1300 K using a high temperature X-ray diffraction method, and the following remarks were obtained.

(1) The lattice parameter of NpO_2 at high temperatures was expressed as

$$a_T\ (\mathrm{pm}) = 542.03 + 4.28 \times 10^{-3}T + 9.07 \times 10^{-7}T^2 - 1.36 \times 10^{-10}T^3.$$

The present values of a_T were about 0.1 pm higher than Taylor's results. The lattice parameters of ThO_2 and PuO_2 at elevated temperatures were in good agreement with Taylor's results. However, the lattice parameters of UO_2 obtained in this study were higher than those reported by Taylor, presumably due to the difference of the reference lattice parameter at 298 K.

(2) The reliable thermal expansion of NpO_2 was determined on the basis of excellent reproducible data of a_T. Thermal expansions of the other actinide dioxides showed good agreement with the recommended literature data.

(3) The linear thermal expansion coefficients (α) calculated at 1200 K were in inverse relation to their melting points. At room temperature, on the other hand, the α value of UO_2 was found to be higher than those of the other actinide dioxides, probably due to lower Debye temperature of UO_2.

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