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Mass-spectrometric determination of oxygen potential of hypostoichiometric urania–yttria solid solution

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Abstract

The oxygen potentials of hypostoichiometric urania–yttria solid solutions expressed as nearly $U_{1-y}Y_yO_{2-x}$ ($x = y/2$) are investigated by use of a mass spectrometer combined with Knudsen cell. The pertinent ions observed in this study were UO_2^+, UO^+ and U^+. The ions associated with yttrium atoms were not observed up to about 2200 K. The partial pressures of uranium-bearing vapor species over the solid solutions were determined by comparing their ion intensities to those of UO_2^+ for UO_2 specimen. It was found that the oxygen potentials of $U_{1-y}Y_yO_{2-x}$ ($x = y/2$) are almost in agreement with those for pure urania having the same oxygen deficiencies.

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1. Introduction

Urania forms a fluorite type solid solution with yttria as well as with other trivalent rare earth oxides. When $YO_{1.5}$ reacts with stoichiometric UO_2 without oxygen pick-up, a fully reduced solid solution $U_{1-y}Y_yO_{2-x}$ ($x = y/2$) having a high concentration of oxygen vacancy in the anion sublattice and U^{4+} and Y^{3+} ions distributed in the cation sublattice is formed [1]. However, the vacancy concentration incorporated in the solid solution is likely to be very sensitive to oxygen partial pressure. In a range of moderate oxygen partial pressures, the vacancies are filled by oxygen atoms, accompanied with a partial promotion of U-valency from 4+ to 5+. Further oxidation induces interstitial oxygen in the crystal, leading to formation of hyperstoichiometric $U_{1-y}Y_yO_{2+x}$ solid solution.

Many reports on oxygen potential of fluorite type solid solution between urania and trivalent rare earth oxides have been published [2–15]. Experimental results show that the solid solutions containing trivalent ions, M^{3+}, generally have higher oxygen potentials than the pure urania. As pointed out in the review by Lindemer and Sutton [10], however, the data of the hypostoichiomtric solid solutions show considerable discrepancies among several investigators. The present work concerns mass-spectrometric measurements on the evaporation of hypostoichiometric urania–yttria solid solutions expressed as nearly $U_{1-y}Y_yO_{2-x}$ ($x = y/2$).

2. Experimental

In Table 1, the compositions and the lattice parameters of the specimens used in this experiment are shown. The method to prepare and characterize the solid solutions is the same as that in Refs. [16,17]. Specimens R9 and R12 contain a large amount of oxygen vacancies were prepared by sintering the pressed compacts of the

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Table 1
Specimens used for vapor pressure measurement

Specimen number	$YO_{1.5}$ content (mol%)	U(VI)/U(IV) ratio (%)	Calculated O/(U + Y) ratio	Determined chemical formula	Lattice parameter (nm)
R9	8.96	1.24	1.966	$U_{0.91}Y_{0.09}O_{1.966}$	0.54576
R12	12.00	1.19	1.950	$U_{0.88}Y_{0.12}O_{1.950}$	0.54555

UO_2 and $YO_{1.5}$ mixtures in hydrogen at 2073 K. The yttria concentration was determined by the anion exchange-EDTA titration method [18]. The U(VI)/U(IV) ratio was determined spectrophotometrically after dissolving the specimens in strong phosphoric acid, where U(VI) was produced from the disproportionation of U(V) in the acid. The O/M ratio was calculated from two quantities, i.e. the yttria concentration and the U(VI)/U(IV) ratio.

The vapor pressure over the solid solution was determined using a quadrupole mass spectrometer equipped with a Knudsen cell. The details of the apparatus were described elsewhere [19]. The Knudsen cell used was made of tungsten with an orifice diameter of 0.5 mm. The temperature of the sample was measured by two sets of W/Re thermocouples inserted into the upper and lower positions of the cell. Using an electron multiplier and moving a shutter allowed us to determine the molecular flow from the orifice. Ion intensities obtained for the vapor phase were calculated to give partial pressures by the reference method which is described in detail later. As the reference material, UO_2 was chosen.

The pertinent ions observed at ionizing electron energy above about 15 eV were UO_2^+, UO^+ and U^+. The ions associated with yttrium atoms were not observed up to about 2200 K. The lowest ionizing electron energy of the present instrument available for this purpose was 7 eV. Since it was not possible to obtain the whole ionization efficiency curves for UO_2^+, UO^+ and U^+ ions, extrapolation of the ionization efficiency curves was made for these ions, which gave the appearance potentials to be in the range of 5–6 eV. Inspection of the ionization curves revealed that the fragmentation of uranium oxide ions to lower oxides or elementary uranium ions occurred significantly at higher electron energies. To avoid the mixing of the fragmentary ions, the ion intensities of UO_2^+, UO^+ and U^+ were measured at 8 eV which was about 2.5 eV above the appearance energies of these ions.

The results of the mass-spectrometric measurement were analyzed under the condition that no significant change of stoichiometry in the sample occurred during the measurements. Then, the mass-spectrometric measurements were performed in the heating step and the duration of the measurement for one sample was restricted within several hours at the longest.

3. Results and discussion

3.1. Vapor pressures over $UO_2(s)$ and $U_{1-y}Y_yO_{2-x}(s)$

Fig. 1 shows the temperature dependence of *IT* values (product of ion intensity and absolute temperature) for UO_2^+ over $UO_{2.003}$. The predominant species in the vapor phase was UO_2^+ along with lesser amounts of UO^+. The open circles in the figure show the *IT* values for UO^+. The heat of evaporation for $UO_2(g)$ determined from the gradient of $\log IT$ against $1/T$ is 585.5 ± 3.8 kJ/mol. This value agrees well with the heat of sublimation reported previously, 590.0 ± 4.8 kJ/mol by Pattoret et al. [20] and 592.2 kJ/mol by Ackermann et al. [21]. Our *IT* values for UO_2^+ related with the partial pressures $p(UO_2)$ over UO_2 reported previously gave a proportionality constant, *K*, in the relation $p(UO_2) = KIT$. In the right side of ordinate in Fig. 1, the unit of partial pressure, Pa, is used. In this case, the constant *K* was obtained by use of $p(UO_2)$ reported by Ackermann et al. [21] at 2000 K.

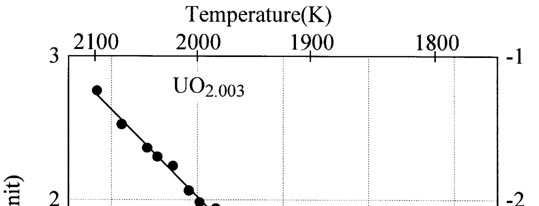

Fig. 1. Temperature dependence of *IT* values for UO_2^+ over UO_2(s). UO_2(s) is used as reference material to convert *IT* values to partial pressures. In the right side of ordinate, the unit of partial pressure is shown together.

The constant K includes ionization cross section and electron multiplier efficiency, which are specific for vapor species beside the apparatus constant. Thus, strictly speaking, the same constant K for UO_2^+ could not be applied to other vapor ions. At the present work, however, the constant was used for the other vapor ions from the reason described below. The cross section for inorganic molecule is, if unknown, often given by summing the theoretical cross sections of the atoms composing the molecule. As the theoretical cross section of U ion is much larger than that of O ion, those of U^+, UO^+ and UO_2^+ can be evaluated to be practically the same. For electron multiplier efficiency, the difference of the cross sections ranging for the species from U^+ to UO_2^+ should be within 10%, since the efficiency of secondary electron multiplier is proportional to the inverse square root mass of ion in general. Assuming that both the cross section and multiplier efficiency are hardly varied through U^+ to UO_2^+, the constant K for UO_2^+ could be applicable to other uranium-bearing ion species.

The partial pressures, converted from IT values using the above K, of vapor species over the solid solution specimens are shown against reciprocal temperature in Figs. 2 and 3. The gaseous species were mainly UO_2^+ and UO^+ over the reduced solid solutions as shown in these figures. Elementary uranium ion, U^+, was also identified over the solid solution containing a large amount of oxygen vacancies, as shown in Fig. 3.

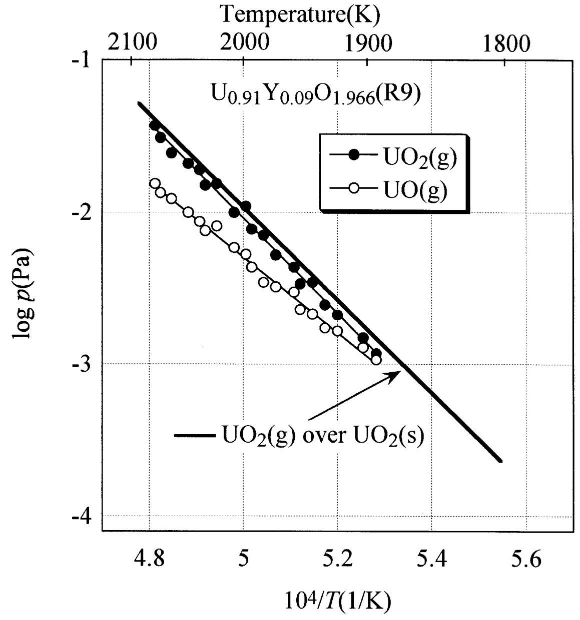

Fig. 2. Temperature dependence of partial pressures of $UO_2(g)$ and UO(g) over specimen R9, together with those of $UO_2(g)$ over $UO_2(s)$.

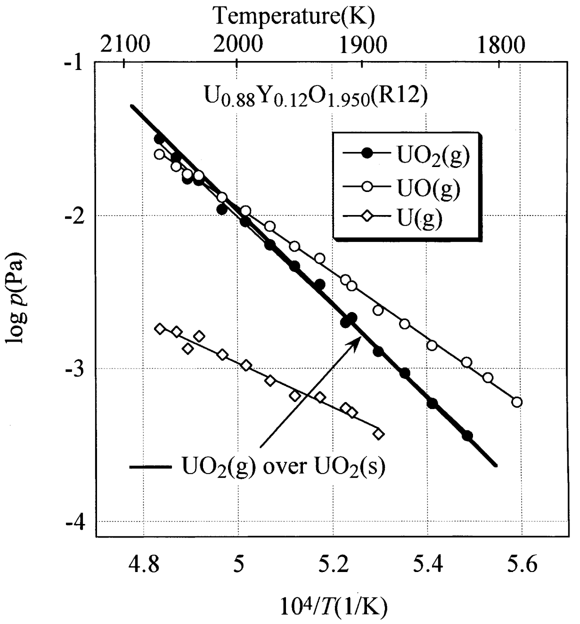

Fig. 3. Temperature dependence of partial pressures of $UO_2(g)$, UO(g) and U(g) over specimen R12, together with those of $UO_2(g)$ over $UO_2(s)$.

From the ion intensities of $I(U)$, $I(UO)$ and $I(UO_2)$ for R12 specimen and the relation of $p(UO_2) = KIT$, the third law enthalpy change, ΔH^0(Eq. (1), 298 K), for the following equilibrium equation,

$$2UO(g) = UO_2(g) + U(g) \tag{1}$$

can be given as

$$\begin{aligned}\Delta H^0(\text{Eq. (1)}, 298\ \text{K}) &= -RT\ln[p(UO_2)p(U)/p(UO)^2] \\ &\quad + T[\text{fef}(UO_2,g) + \text{fef}(U,g) \\ &\quad - 2\text{fef}(UO,g)] \\ &= -RT\ln[I(UO_2)I(U)/I(UO)^2] \\ &\quad + T[\text{fef}(UO_2,g) + \text{fef}(U,g) \\ &\quad - 2\text{fef}(UO,g)],\end{aligned}$$

where $\text{fef} = -[G^0(T) - H^0(298\ \text{K})]/T$. The values of ΔH^0(Eq. (1), 298 K) determined by use of fefs for $UO_2(g)$, UO(g) and U(g) [22] are plotted against temperature in Fig. 4. The ΔH^0(Eq. (1), 298 K) value obtained is −12.6 kJ/mol.

The enthalpy change in Eq. (1) is also obtained as

$$\begin{aligned}\Delta H^0(\text{Eq. (1)}, 298\ \text{K}) &= \Delta H_f^0(U, g, 298\ \text{K}) \\ &\quad + \Delta H_f^0(UO_2, g, 298\ \text{K}) \\ &\quad - 2\Delta H_f^0(UO, g, 298\ \text{K}).\end{aligned}$$

With 533.0, 43.6 and −466.6 kJ/mol [22] for $\Delta H_f^0(U, g, 298\ \text{K})$, $\Delta H_f^0(UO, g, 298\ \text{K})$ and ΔH_f^0(UO_2,

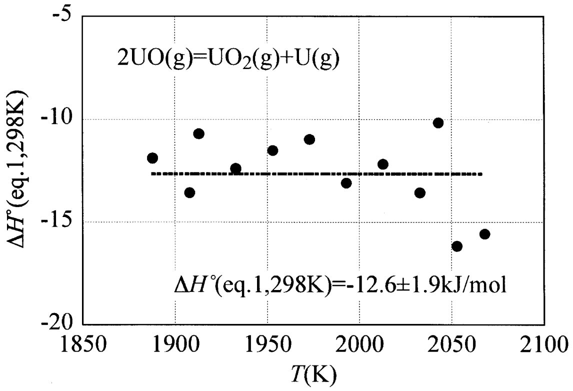

Fig. 4. The third law enthalpy for the reaction; $2UO(g) = UO_2(g) + U(g)$.

g, 298 K), respectively, −20.8 kJ/mol is given as ΔH^0(Eq. (1), 298 K). The error of this ΔH^0(Eq. (1), 298 K) is considered to be larger than 10 kJ/mol according to the reference values [22], where the errors of $\Delta H_f^0(U, g, 298\ K)$, $\Delta H_f^0(UO, g, 298\ K)$ and $\Delta H_f^0(UO_2, g, 298\ K)$ are considered to be within 1%, 10% and 5%, respectively. Then, the 8.2 kJ/mol difference in these two ΔH^0(Eq. (1), 298 K) values is within the error, in the other word, the assumption of the same constant K for all uranium-bearing vapor species is correct.

3.2. Oxygen potential of $U_{1-y}Y_yO_{2-x}(s)$

For determining oxygen partial free energy or oxygen potential, $\Delta\overline{G}(O_2)$, of the compounds studied in this work, it was necessary to calculate the equilibrium oxygen partial pressure, $p(O_2)$. In the present work, $p(O_2)$ was deduced as follows. Considering the following equilibria in gas phase,

$$UO(g) = U(g) + 1/2O_2(g), \tag{2}$$

$$UO_2(g) = U(g) + O_2(g) \tag{3}$$

and

$$UO_2(g) = UO(g) + 1/2O_2(g), \tag{4}$$

$p(O_2)$ associated with Eq. (4) for specimens R9 and R12 can be obtained using the following relation,

$$\begin{aligned}\Delta H^0(\text{Eq. (4)}, 298\ \text{K}) &= -RT\ln[p(O_2)^{1/2}p(UO)/p(UO_2)] \\ &\quad + T[1/2\,\text{fef}(O_2, g) + \text{fef}(UO, g) \\ &\quad - \text{fef}(UO_2, g)] \\ &= -RT\ln[p(O_2)^{1/2}I(UO)/I(UO_2)] \\ &\quad + T[1/2\,\text{fef}(O_2, g) + \text{fef}(UO, g) \\ &\quad - \text{fef}(UO_2, g)].\end{aligned}$$

Then, $p(O_2)$ values for specimens R9 and R12 are obtained by Eq. (4) with the use of the reported values of standard enthalpies of formation and fefs for $UO_2(g)$, $UO(g)$ and $O_2(g)$ [22] and the measured pressures of $UO_2(g)$ and $UO(g)$ shown in Figs. 2 and 3. Further, $p(O_2)$ values for specimen R12 are also obtained by Eq. (2) or (3) in the similar manner.

The above oxygen potentials can also be obtained using the partial pressures of the uranium-bearing vapor species other than $UO_2(g)$ and the activities of UO_2 in the solid solutions which can be evaluated from the relative values of partial pressures of $UO_2(g)$ over the solid solutions to those over pure urania. These activities, however, are not precise due to the uncertainty of the absolute pressures of the vapor species estimated from their ion currents. Thus, the determination of the oxygen potential evaluated in this manner was not carried out.

In Fig. 5 are shown the temperature dependence of $\Delta\overline{G}(O_2)$ directly deduced from the relation $\Delta\overline{G}(O_2) = RT\ln p(O_2)$. The numerical expression of $\Delta\overline{G}(O_2)$ in joule unit is as follows.

For specimen R9,

$$\Delta\overline{G}(O_2) = -1\,262\,000 \pm 42\,300 - (-287.3 \pm 11.13)T, \tag{5}$$

for specimen R12 from Eq. (2),

$$\Delta\overline{G}(O_2) = -1\,224\,000 \pm 21\,200 - (-264.0 \pm 10.70)T, \tag{6}$$

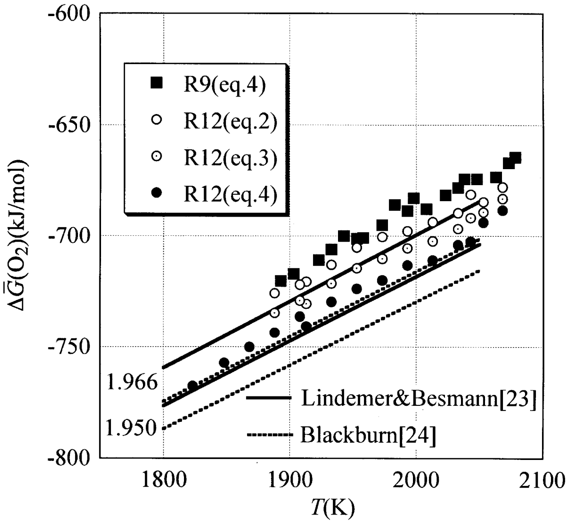

Fig. 5. Temperature dependence of $\Delta\overline{G}(O_2)$ for urania–yttria solid solutions together with that for pure urania evaluated from the models of Lindemer and Besmann [23] and Blackburn [24].

for specimen R12 from Eq. (3),

$$\Delta\overline{G}(O_2) = -1\,259\,000 \pm 16\,070 - (-277.7 \pm 8.109)T \tag{7}$$

and for specimen R12 from Eq. (4),

$$\Delta\overline{G}(O_2) = -1\,310\,000 \pm 16\,400 - (-299.4 \pm 8.390)T. \tag{8}$$

The $\Delta\overline{G}(O_2)$ values for R12 deduced by Eqs. (2) and (3) are almost the same as those by Eq. (4) considering the uncertainty of the thermodynamic quantities used for calculation. In Fig. 5, the temperature dependences of $\Delta\overline{G}(O_2)$ for UO_{2-x} presented by Lindemer and Besmann [23] and Blackburn [24] are also shown as the solid and dotted lines, respectively. From this figure, it is seen that the $\Delta\overline{G}(O_2)$ values obtained in this study are almost in agreement with those for pure urania at the same x.

3.3. Partial molar entropy and enthalpy of $U_{1-y}Y_yO_{2-x}(s)$

From the temperature dependence of $\Delta\overline{G}(O_2)$, the partial molar entropy $\Delta\overline{S}(O_2)$ and the partial molar enthalpy $\Delta\overline{H}(O_2)$ of oxygen are calculated by least-squares method using the following thermodynamic relationships

$$\Delta\overline{S}(O_2) = -\partial\Delta\overline{G}(O_2)/\partial T$$

and

$$\Delta\overline{H}(O_2) = \Delta\overline{G}(O_2) + T\Delta\overline{S}(O_2).$$

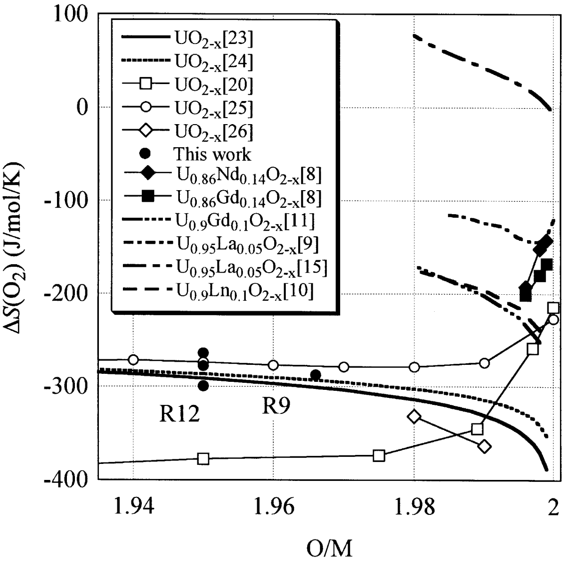

Fig. 6. Variation of $\Delta\overline{S}(O_2)$ for urania–yttria solid solutions with O/M ratio compared with $\Delta\overline{S}(O_2)$ for pure urania and various other solid solutions with about 10% foreign trivalent cations.

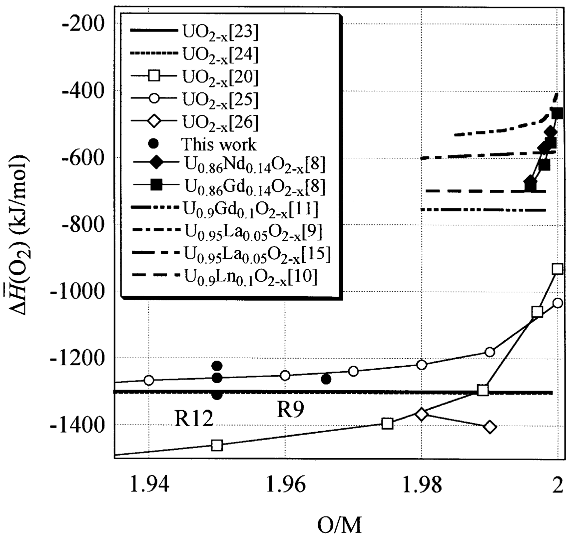

Fig. 7. Variation of $\Delta\overline{H}(O_2)$ for urania–yttria solid solutions with O/M ratio compared with $\Delta\overline{H}(O_2)$ for pure urania and various other solid solutions with about 10% foreign trivalent cations.

These calculated values are shown in Figs. 6 and 7, respectively. For comparison, these figures also include the experimental and theoretical values for pure urania [20,23–27] and the M^{3+} solid solutions containing about 10% foreign cations [2,7–11,15]. Some of the theoretical values are calculated here from the reference $\Delta\overline{G}(O_2)$ using the above relations. As shown in these figures, the thermodynamic quantities obtained in this study are in good agreement with those for pure urania. These results are much different from those deduced from some models [10,11,15] which indicate that both the $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$ values for the hypostoichiomtric M^{3+} solid solutions are much higher than those for the pure urania. However, the reduced specimens studied in this work are considered to be mainly constituted of Y^{3+} and U^{4+} cations and their respective concentrations are the same as those of U^{3+} and U^{4+} of the hypostoichiometric pure urania having the same x value. If the distribution of these cations and oxygen vacancies in the cation and anion sublattices is identical to that for pure urania, the configurational entropy for the reduced specimen should be in accord with that for pure urania. So their $\Delta\overline{S}(O_2)$ values can be in good agreement each other since the configurational entropy is considered to be the principal cause of variation of $\Delta\overline{S}(O_2)$ with x [28]. While we do not know why the little difference of the $\Delta\overline{H}(O_2)$ values between the reduced specimens and pure urania arises. But the fluorite type pure urania and its solid solutions are regarded as ionic crystals in which the Coulomb interaction principally contributes to cohesive energy. If the reduced specimens have the same distribution of cations and anions and the same distances among these ions as pure urania, their cohesive energies should be in agreement each other. So the $\Delta\overline{H}(O_2)$ values for the reduced specimens may also approach to those for pure urania.

The large differences of $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$ values between the M^{3+} solid solutions and pure urania indicated by several authors are still not quantitatively elucidated. Then, further experiments and theories for M^{3+} solid solutions are required for understanding the characteristics in detail.

4. Conclusion

The oxygen potentials of hypostoichiometric urania–yttria solid solutions expressed as nearly $U_{1-y}Y_yO_{2-x}$ $(x = y/2)$ were determined by Knudsen-effusion mass-spectrometric method. The oxygen potentials obtained in this work are almost in agreement with those for pure urania having the same oxygen deficiencies. Further, the partial molar entropies and the partial molar enthalpies of oxygen are also in agreement with those for the pure urania having the same hypostoichiometric composition.

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