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# Oxidation-Reduction Properties of Mixed Oxides in the Cerium-Uranium-Oxygen System

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The formation and the oxidation-reduction properties of mixed oxides in the Ce–U–O ternary system were examined by means of thermogravimetry and the X-ray diffraction technique. The mixed oxides were prepared by the reactions of $CeO_2$ with $U_3O_8$ in air and in hydrogen. The composition of the products heated in air, followed by slow cooling to room temperature, was approximately expressed by this equation: $y\mathrm{CeO_2}+(1-y)\mathrm{UO_{2.67}}$. By X-ray diffraction, it was shown that the oxides formed at 1100 °C in air were mixtures of $Ce_{0.6}U_{0.4}O_{2.3}$ and $\alpha$-$U_3O_8$ in the $y<0.6$ range, while they were in single phases of solid solutions for $y\geq0.6$. When the mixed oxides, $MO_{2+x}$, where M indicates $y\mathrm{Ce}+(1-y)\mathrm{U}$, were re-heated in air, weight loss due to oxygen liberation was observed above 500 °C, and it was enhanced with a rise in the temperature. The hydrogen reduction of the oxides proceeded in two steps; the first step was the reduction of $MO_{2+x}$ to $MO_2$ below 600 °C, and the second one was the reduction of $MO_2$ to $MO_{2-x}$ above 600 °C. The composition of the oxides obtained can be given by this equation: $y\mathrm{CeO_{1.81}}+(1-y)\mathrm{UO_{2.00}}$. Two separate linear relationships for the lattice parameter of the fluorite-type structure as a function of the cerium content were obtained; one is applicable to the solid solutions with $y\leq0.6$, where the lattice parameter is nearly that of $UO_2$, and the other to the solid solutions with $y\geq0.4$. The latter obeys Vegard's law between $UO_2$ and $CeO_2$. The oxides with $y=0.4$—$0.6$ were in the two-phase region of the solid solutions.

In the cerium-uranium-oxygen system, it has been shown that there exists a homogeneous region of the solid solution with a fluorite structure. Several workers[1–8] have investigated its composition range, lattice parameter, and thermodynamic properties. A phase diagram of the system at 900 °C was first drawn by Hoch and Furman[4] from the data of Hund[1] and the results of their own quenching experiments. Later, Markin *et al.*[5] constructed a phase diagram between $UO_2$–$U_3O_8$ and $CeO_2$–$CeO_{1.81}$ for temperatures between room temperature and 600 °C using the results obtained by the high temperature X-ray diffraction technique. In spite of their experiments, however, the literature data on the phase relations and the chemical properties seem still to be incomplete.

Cerium is produced in nuclear fuels as one of the fission products of high yields. The knowledge of the Ce–U–O ternary system is, therefore, of basic importance for investigating the irradiation behavior of uranium dioxide fuel in connection with the changes in the phase relations and in the thermodynamic properties caused by accumulated fission products. In addition, cerium is often used in simulation studies of plutonium, a promised fissile material in fast breeder reactor, because of their similar chemical and/or thermodynamic behavior. Therefore, the investigation of this ternary system would contribute to our knowledge of the phase behavior of the Pu–U–O system, too. The physical and chemical properties as well as the phase relations of the Ce–U–O system have, nevertheless, not been systematically studied. In the present experiment, we investigated the formation and the oxidation-reduction properties of the mixed oxide of the Ce–U–O ternary system by means of thermogravimetry and the X-ray diffraction technique. The literature data on the lattice parameter, which were rather scattered, were also re-examined.

## Experimental

*Materials.* $CeO_2$ of a 99.99% purity was provided by the Shin-etsu Chemical Co. Ltd. The oxide was heated at 1000 °C in air for 3 h before use. $U_3O_8$ was prepared by heating ammonium diuranate at 900 °C in air for 24 h. Both compounds were weighed so that the cerium contents were 0.10, 0.20, 0.27, 0.40, 0.50, 0.60, and 0.80 atom% in the respective mixtures. Mixing was done in an agate mortar, and the mixtures were compacted at $3\times10^8$ Pa into cylindrical pellets 10 mm in diameter and about 2 mm thick. The weight of each pellet was about 800 mg.

*Apparatus and Procedures.* The experiments were mainly carried out by the use of the thermogravimetric technique. The apparatus consists of a Cahn Model-RH electrobalance, a pressure-measurement system, a gas-supply system, and vacuum pumps. The balance was adjusted so as to have a maximum weight change of 500 mg and a sensitivity of 0.01 mg. A fused quartz crucible, 20 mm in height and 18 mm in outer diameter, was suspended from the balance. Then, a quartz reaction tube, 26 mm in outer diameter and 310 mm in length, was connected to the vessel containing the balance. After the reaction system had been evacuated to $10^{-1}$ Pa, the sample was weighed. The system was then filled with air (or hydrogen in the reduction experiments) and the temperature was raised. Hydrogen from the cylinder was used after having been purified by passage through palladium asbestos heated at 300 °C and through a liquid-nitrogen trap. The weight change due to buoyancy and convection was corrected by using a platinum wire. The sample was weighed again in a vacuum after the reaction.

The temperature of the sample was measured with a Pt/Pt+13%Rh thermocouple placed close to the crucible inside the reaction tube. The furnace temperature was automatically controlled so as to be raised at a constant heating rate or to be held at a desired point. The experiments were made at the heating rate of 2 °C/min.

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*X-Ray Analysis.* The samples were finely ground, loaded into capillaries, and then vacuum-sealed. The X-ray photographs were obtained with a Norelco 114.6 mm camera using nickel-filtered Cu $K\alpha$ radiation. The lattice parameters were obtained by least-squares calculations for the diffraction lines at higher angles.

## Results and Discussion

*Formation of Mixed Oxides in Air.* The reaction of $CeO_2$ with $U_3O_8$ was examined by heating mixture pellets with various cerium contents from room temperature to 1100 °C in air. After the temperature had been raised to 1100 °C, the sample was held at that temperature for 3 h; then it was slowly cooled. When heated in air, $U_3O_8$ began to lose oxygen at about 890 °C, and the O/U ratio was lowered from 2.667 to 2.653 at 1100 °C. On the other hand, the weight loss of $CeO_2$ was not observed up to 1100 °C. For the mixtures of $CeO_2$ and $U_3O_8$, it was found that the weight loss occurred at slightly lower temperatures than that of $U_3O_8$ in any mixing ratio. The weight loss at high temperatures was augmented by $y$, which suggests a reaction between $CeO_2$ and $U_3O_8$, the mixed oxide thus formed being oxygen-deficient compared with the initial bulk composition of the sum of $y\mathrm{CeO_2}+((1-y)/3)\mathrm{U_3O_8}$. While the sample was held at 1100 °C for 3 h, the O/M ratio decreased slightly with time; here, M indicates $y\mathrm{Ce}+(1-y)\mathrm{U}$. The X-ray patterns of these oxides showed that the products were mixtures of $\alpha$-$U_3O_8$ and solid solution for $y=0$—$0.5$, and homogeneous solid solutions for $y\geq 0.6$.

*Formation of Mixed Oxides in Hydrogen.* The reduction of $U_3O_8$ with hydrogen began at about 330 °C and finished at 630 °C. The product was $UO_{2.000}$. On the other hand, the reduction of $CeO_2$ with hydrogen began at 550 °C, and then the O/Ce atom ratio gradually decreased with an increase in the temperature. The O/Ce ratio was 1.815 at 1000 °C, and it was hardly changed even after the sample was kept at that temperature for 3 h. As for the mixtures of $CeO_2$ and $U_3O_8$, the weight loss began at about 330 °C, the initiation temperature of the reduction of $U_3O_8$, for any mixing ratio. When the sample was heated further, a plateau appeared on the TG curve around the O/M ratio of 2.02 at temperatures between 600 and 650 °C. Above 650 °C the O/M ratio was seen to decrease again with increasing temperature. This reaction behavior of the $CeO_2$ and $U_3O_8$ mixtures in hydrogen atmosphere is very similar to that of the solid solution, as will be stated below.

*Hydrogen Reduction of the Mixed Oxides Prepared in Air.* Typical TG curves for the reduction of $U_3O_8$, $CeO_2$, and the mixed oxides are shown in Fig. 1. The mixed oxides were prepared by heating mixtures of $CeO_2$ and $U_3O_8$ at 1100 °C for 3 h in air. As may be seen in the figure, the mixed oxides were reduced to an O/M ratio of nearly two by heating up to 600 °C. Then, the plateau appeared in the temperature range between 600 and 650 °C, after which the specimens were again reduced, but at slower rates. From this fact, it is deduced that the oxides with O/M >2 are reduced more easily than those with O/M<2. This is related to the thermodynamic properties of the solid solution. Thermodynamic studies of $MO_{2\pm x}$[4,6] show that the curve of the partial molar Gibbs energy of oxygen, $\Delta\overline{G}_{O_2}(MO_{2\pm x})$, against $x$ for any $y$ value changes from a large negative value at O/M<2 to a small negative value at O/M>2 in a sigmoid shape. The large change in $\Delta\overline{G}_{O_2}$ occurs in the vicinity of the stoichiometric composition, O/M≈2. As the Gibbs energy of formation of water, $\Delta G^\circ_f(H_2O)$, is close to $\Delta\overline{G}_{O_2}(MO_{\approx 2})$ at temperatures from 600 to 1000 °C, it is reasonable to suppose that the solid solution is readily reduced with hydrogen to the composition with O/M≈2. The reduction of the solid solution proceeds by removing the produced water vapor.

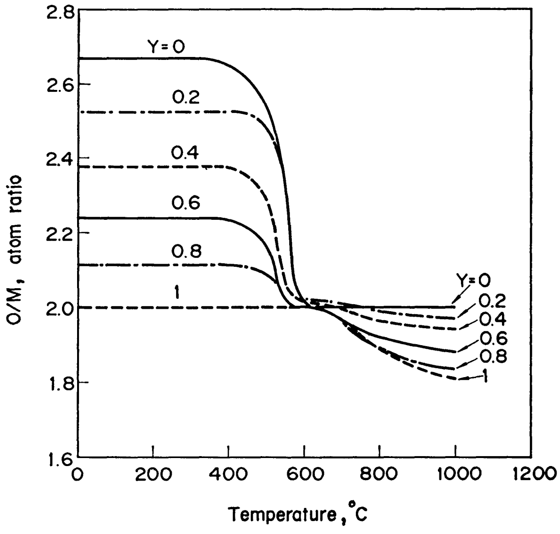

Fig. 1. TG curves for reduction of the mixed oxides $MO_{2+x}$ in hydrogen atmosphere.
Heating rate: 2 °C/min, y: Ce/(Ce+U) ratio.

The X-ray pattern of the product showed that it was a two-phase mixture with the fluorite-type structure for $0.4\leq y\leq 0.6$, and a single-phase product with the fluorite-type structure for $y\leq 0.3$ and $y>0.6$. The O/M ratio and the lattice parameter of the mixed oxide thus formed are shown in Table 1.

*Air Oxidation of the Mixed Oxides Prepared in Hydrogen.* Figure 2 shows some typical TG curves for the oxidation of the mixed oxides in air. The mixed oxides used here were prepared by reducing mixtures of $CeO_2$ and $U_3O_8$ with hydrogen in situ in a quartz crucible at 1000 °C for 3 h. In a series of experiments to check the completeness of mixing, the reduced pellets were crushed, intimately mixed, and then recompacted into pellets which were used for oxidation. When air was re-introduced into the reaction vessel after evacuation, the sample was slowly oxidized to the O/M ratio of nearly two even at room temperature. This oxidation reaction was accelerated by heating. For the oxidation of $UO_2$, the formation of $U_3O_7$ as the intermediate phase was seen on the TG curve. This bend was observed in the oxides of $y=0.1$—$0.4$. Every TG curve for the oxidation of $MO_{2-x}$

TABLE 1. COMPOSITIONS, PHASES, AND LATTICE PARAMETERS OF THE MIXED OXIDES

| $y$ | Oxidized in air at 1100 °C | | | Reduced in hydrogen at 1000 °C | | |
|---|---|---|---|---|---|---|
| | O/M ratio | Phase | Lattice parameter/Å | O/M ratio | Phase | Lattice parameter/Å |
| 0 | 2.667 | $\alpha$-$U_3O_8$ | $a$=6.7313<br>$b$=11.958<br>$c$=4.1451 | 2.000 | $UO_2$ | 5.4700 |
| 0.10 | 2.594 | $\alpha$-$U_3O_8$+s.s. | 5.433 | 1.981 | fcc | 5.4701 |
| 0.20 | 2.533 | $\alpha$-$U_3O_8$+s.s. | 5.428 | 1.982 | fcc | 5.4696 |
| 0.27 | 2.479 | $\alpha$-$U_3O_8$+s.s. | 5.424 | | | |
| 0.40 | 2.379 | $\alpha$-$U_3O_8$+s.s. | 5.423 | 1.945 | fcc | 5.4675(strong)<br>5.44—5.45(weak) |
| 0.50 | 2.320 | $\alpha$-$U_3O_8$+s.s. | 5.423 | 1.914 | fcc | 5.4683(strong)<br>5.4412(weak) |
| 0.60 | 2.24 | fcc | 5.4269 | 1.899 | fcc | 5.4646(weak)<br>5.4372(strong) |
| 0.80 | 2.115 | fcc | 5.4192 | 1.857 | fcc | 5.4237 |
| 1 | 2.000 | $CeO_2$ | 5.4111 | 1.815 | $CeO_{2-x}$ | |

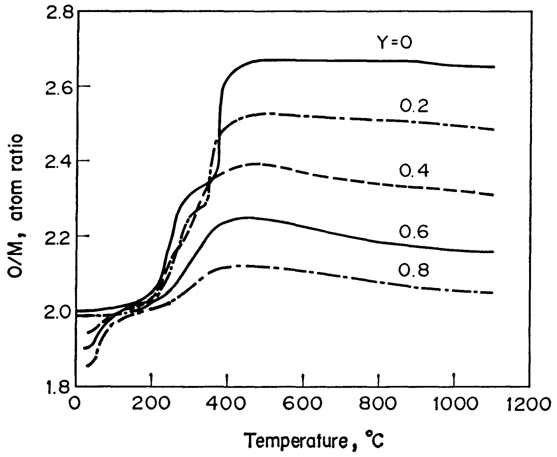

Fig. 2. TG curves for oxidation of the mixed oixdes $MO_{2-x}$ in air.
Heating rate: 2 °C/min, y: Ce/(Ce+U) ratio.

showed a maximum of the O/M ratio at temperatures between 450 and 500 °C. Above 500 °C, the oxides began to lose their oxygen. The decrease in the O/M ratio was enhanced with a rise in the temperature. When the oxides were cooled from higher temperatures than the temperature giving the maximum O/M ratio, the O/M value increased on the line of the heating process up to the maximum O/M ratio, and the value was maintained unchanged on a further lowering of the temperature.

The X-ray pattern of the product revealed that it was a mixture of $\alpha$-$U_3O_8$ and the solid solution for $y \leq 0.5$, and was in the single phase of the solid solution for $y \geq 0.6$. For the product of the $y$ values between 0.1 and 0.5, the X-ray intensity of the diffracted $\alpha$-$U_3O_8$ lines was weakened with the increase in the cerium content. Although the $U_3O_8$ phase which was formed accompanying the solid solution has been reported to be in the $\beta$ modification,[7] it was identified as $\alpha$-$U_3O_8$ by the present analysis of the X-ray patterns. The O/M ratio, phase, and lattice parameter for the product slowly cooled from 1100 °C in air are shown in Table 1. It may be seen that the lattice parameter of the cubic fluorite phase remains constant regardless of the cerium content between $y$=0.1 and 0.5. The products of $y$=0.6 and 0.8 were found to be in a single phase with the fluorite-type structure, and their lattice parameters were lowered with an increase in the cerium content.

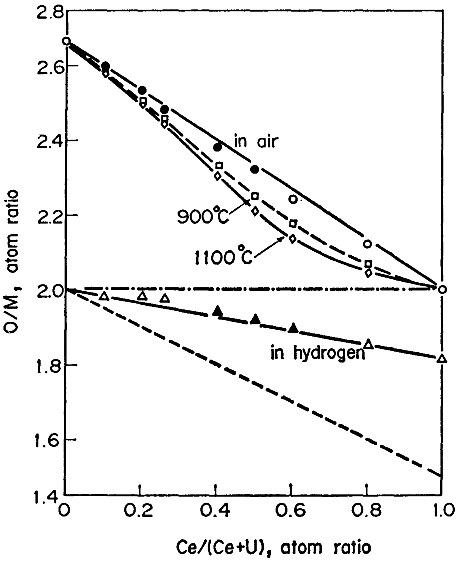

Fig. 3. Variation of the O/M atom ratio of the mixed oxides as a function of cerium concentration.
●: Two-phase mixture below 500 °C in air, ○: single phase below 500 °C in air, □: O/M ratio of the mixed oxides at 900 °C in air,' ◇: O/M ratio of the mixed oxides at 1100 °C in air, △: single phase in hydrogen, ▲: two-phase mixture in hydrogen.

*Valence State of Uranium and Cerium in the Mixed Oxides.* Figure 3 shows the O/M ratio *vs.* Ce/M ratio for the samples prepared under various reaction conditions. The straight line connecting the circles represents the O/M ratio of the oxides heated in air at 1100 °C, followed by annealing to room temperature. The open circles indicate a single phase, and the filled circles, a two-phase mixture. The other marks represent the

O/M ratio of the samples heated at 900 and 1100 °C in air. The figure shows that the mixed oxide prepared in air is the single phase with a fluorite structure at least below the O/M ratio of 2.24. In the U–O system, the phase diagram shows that the composition range of the fluorite phase extends to $O/U=2.25$. The O/M ratios of the samples which were obtained by reducing the mixed oxides in a hydrogen atmosphere at 1000 °C for 3 h and then slowly cooling them to room temperature are indicated by △ and ▲ in the same figure, where open and filled marks indicate single-phase and two-phase, respectively. All the oxides prepared in hydrogen had the fluorite structure. The oxides for $y=0.4$—0.6 consisted of two phases with different lattice parameters. The O/Ce atom ratio of the cerium oxide reduced by hydrogen was 1.815, the same as the ratio reported by Markin *et al.*[5]

For the mixed oxides prepared in air, the O/M ratios of the oxides below 500 °C decrease nearly linearly from 2.667 of $U_3O_8$ at $y=0$ to 2.00 of $CeO_2$ at $y=1$. This shows that the mean valence state of uranium, +5.33, is not varied by the dissolution of cerium. On the other hand, the O/M ratios of the oxides at 900 and 1100 °C in air are lower than those of the oxides cooled to room temperature. For example, the O/M ratios of the mixed oxides at 900 °C are 2.18 for $y=0.6$ and 2.07 for $y=0.8$, the mean valence states of uranium being +4.9 and +4.7 respectively, if cerium is regarded as in the +4 state.

The tendency for the valence state of uranium not to vary or, rather, to be diminished, by the addition or cerium is obviously different from the case of the Sr–U–O system.[9] In this system, the valence state of uranium was raised from +5.33 of $U_3O_8$ to +6.00 of $Sr_2UO_5$ with an increase in the content of strontium.

For the mixed oxides prepared in hydrogen, $MO_{2-x}$, the O/M ratio decreases nearly linearly from 2.00 at $y=0$ to 1.815 at $y=1$. This fact shows that the valence state of uranium is +4 and that of cerium is +3.63, neither of which is varied by the Ce/U atom ratio.

*Lattice Parameters of the Mixed Oxides.* The lattice parameters of the mixed oxides prepared in air and in hydrogen are plotted as functions of the cerium content in Fig. 4, together with the data from the literature.[1–5,7]

The oxide prepared at 1100 °C in air is two-phase mixture for $y<0.6$. The constant lattice parameter, 5.426 Å, though scattered, indicates that the mixed oxide is in two phases, $Ce_{0.6}U_{0.4}O_{2.3}+\alpha\text{-}U_3O_8$. The composition of $Ce_{0.6}U_{0.4}O_{2.3}$ was obtained from Fig. 3 using the intersection between the lattice parameter in the two-phase region of $y<0.6$, 5.426 Å, and the straight line in the single-phase region of $y\geq0.6$. The lattice parameter of the mixed oxide with $y\geq0.6$ decreases with an increase in the cerium content.

The lattice parameter in the two-phase region of the mixed oxides prepared in air has been determined by many workers.[1–5,7] Although their results are not in complete agreement, it has been found that the lattice parameter has a tendency to increase with a decrease in the $y$ value. On the other hand, the $y$ value at the phase limit of the fluorite solid solution, as seen in Paul's results,[7] decreases with a rise in the firing temperature. The lattice parameter value is also varied by the cooling conditions; the value of a quenched sample is larger than that of an annealed one. The difference in the lattice parameters in the literature, therefore, may be caused by the heating and cooling conditions.

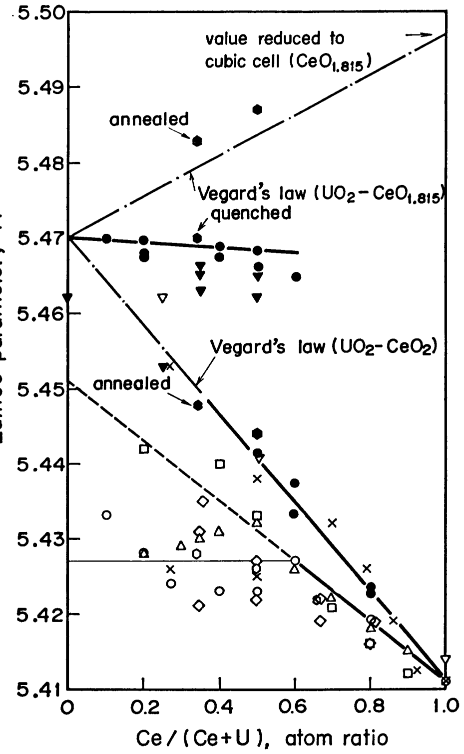

Fig. 4. Lattice parameter of the mixed oxides. □: Hund *et al.*,[1] ◇: Rüdorff and Valet,[2] ×: Zuromsky and Chernock,[3] ▽,▼: Hoch and Furman,[4] O,▮: Markin *et al.*,[5] △: Paul,[7] ○,●: Present work. Open marks and × show the oxides heated in air and filled marks show the oxides heated in hydrogen.

The reported values[1,3,7] of lattice parameters in the single-phase region are all in agreement. It is found that the lattice parameter varies linearly against the cerium concentration, except for the results by Hund *et al.*[1] If the line of the lattice parameter *vs.* Ce/(Ce+U) atom ratio is extraporated to $y=0$, as Rüdorff and Valet[2] have done, 5.451 Å is obtained as the lattice parameter of the cubic uranium oxide. This value is found in the nonstoichiometric region of $U_4O_9$ the mother structure of which is the fluorite. If the relationship between the lattice parameter and the O/U ratio in $U_4O_9$ obtained by Lynds *et al.*[10] is applied, the O/U ratio of the extrapolated uranium oxide becomes 2.18. Markin *et al.*[5] obtained oxides with the fluorite-type or $U_4O_9$-type cubic structure by the partial oxidation of hypostoichiometric oxides, $MO_{2-x}$, to $MO_{2.25}$ for $y<0.4$; their lattice parameters are placed on the broken line.

The variation in the lattice parameter of the solid solutions prepared in hydrogen can be shown by two separate lines. One is the line for $y\leq0.6$, with a lower gradient, while the other is the line for $y\geq0.4$, which follows Vegard's law connecting 5.4700 Å of $UO_2$ and the 5.4111 Å of $CeO_2$. The oxides for $y=$ 0.4—0.6 are two-phase mixtures of fluorite structures with different lattice parameters. Markin *et al.*[5] have reported that a two-phase mixture was formed by the phase separation during very slow cooling to room temperature. The lower lattice-parameter values obey Vegard's law. Therefore, it is considered that the oxides with these smaller values correspond to the hypostoichiometric oxides $MO_{2-x}$ formed between $UO_2$ and $CeO_{2-x'}$, where $2-x'$ is probably much smaller than 1.815.

The larger lattice-parameter values at $y<0.6$ obtained in the present work are in agreement with those by Hoch *et al.*[4] These values are close to the lattice parameter of $UO_2$. On the other hand, the X-ray pattern of $CeO_{1.815}$ showed the single phase of the fluorite structure with the lattice parameter of 5.4111 Å. The phase diagram of the cerium-oxygen system[11—14] shows that there is a miscibility gap between $CeO_2$ and $Ce_{11}O_{20}(CeO_{1.818})$. Although $CeO_{1.815}$ has a rhombohedral structure, the psudocubic lattice parameter calculated from the volume of the rhombohedral cell by Brauer and Gingerich[12] and by Ray *et al.*[14] is 5.497 Å. The lattice parameters in the present work are lower than the line of Vegard's law connecting $UO_2$ and $CeO_{1,815}$, while the data reported by Markin *et al.*[5] are above that line. If our lattice parameters are extrapolated to $y=1$, 5.467 Å is obtained, which corresponds to the $CeO_{1.88}$ of Ray's data.[14]

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