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# Effect of cations on lattice constants of $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th, La) at low doped cation concentrations

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## Abstract

In order to clarify the effect of doped cations on the lattice constants of stoichiometric $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th, La) solid solutions at small $y$, the lattice constants of stoichiometric $(M_yU_{1-y})O_{2.00}$ as a function of doped cation concentration were measured at room temperature by the powder X-ray diffraction method. The lattice constant of stoichiometric uranium dioxide doped with plutonium ions decreased linearly with increasing plutonium concentration up to 20 at%, whereas the lattice constants of the dioxide doped with thorium and lanthanum ions increased linearly with increasing thorium and lanthanum concentration up to 4 and 9 at%, respectively. No abnormal behavior was observed at $y=0.04$ for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ and at $y=0.02$ for stoichiometric $(Th_yU_{1-y})O_{2.00}$, as reported in the literature. The valence of the doped cations is discussed in terms of the dependence of the cation concentration on the lattice constants by assuming a random distribution of doped cations in uranium dioxide and an ionic model where every cation and anion form a rigid sphere.
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## 1. Introduction

Uranium–plutonium mixed oxides have been used as nuclear fuels for fast breeder reactors and plutonium thermal reactors. It has been reported that the lattice constants of uranium–plutonium mixed oxides decrease linearly with increasing plutonium concentration following Vegard's law [1]. However, recent experimental results by Beauvy [2] exhibited divergence from the classical Vegard's law for the stoichiometric oxide up to approximately 5 at% of plutonium, but above 5 at% it was shown to obey Vegard's law. Cohen and Berman [3] also reported that uranium–thorium mixed oxides deviated from Vegard's law at around 2 at% thorium concentration, indicating the formation of some kind of short-range ordering or clustering. However, it is difficult to consider that uranium–plutonium and uranium–thorium mixed oxides form non-ideal solid solutions because uranium, plutonium and thorium dioxides have the same fluorite-type crystal structure and the ionic radii of these cations are equivalent.

The reason for the deviation from Vegard's law at a particular concentration ($y=0.04$ for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ [2] and $y=0.02$ for stoichiometric $(Th_yU_{1-y})O_{2.00}$ [3]) is not yet known. In order to clarify the effect of doped cations on the lattice constants of stoichiometric $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th, La) solid solutions at small $y$, the lattice constants of stoichiometric $(M_yU_{1-y})O_{2.00}$ were measured as a function of doped cation concentration at room temperature using the powder X-ray diffraction method.

## 2. Experimental

Plutonium dioxide was dissolved in 7 M $HNO_3$ containing a low concentration of fluoride ion. The solution was passed through an ion-exchange column of Dowex 1-X4 to remove $^{241}$Am impurity. A portion of the purified plutonium nitrate solution of 5 and 10 at% concentration was mixed with uranium nitrate solution which had been formed by dissolving high purity uranium metal blocks in dilute nitric acid. The mixed solution was gently evaporated and dried in a mantle heater. Mixed oxide powder was obtained by calcining the solid nitrate at 1073 K in air, and then reacted at 1673 K in vacuum. The obtained powder sample was annealed using a flowing 50% CO–50% $CO_2$ gas mixture at 1273 K in order to produce the

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stoichiometric composition. The $(Pu_{0.05}U_{0.95})O_{2.00}$ or $(Pu_{0.1}U_{0.9})O_{2.00}$ powder obtained was mixed with $UO_{2.00}$ powder in the desired composition. The oxide powder was subsequently pressed into a 6 mm diameter circular die at about 20 kg mm$^{-2}$, and the pellet was then sintered in vacuum at 1673 K for 3–4 h. After the pulverizing, mixing, pelletizing and heating procedures had been repeated, the product was then annealed under a flow of 50% CO–50% $CO_2$ gas mixture at 1273 K in order to produce a specimen of stoichiometric composition.

$ThO_2$ (or $La_2O_3$) and $UO_2$ powders were mixed at the desired composition and pressed into a 6 mm diameter circular die at about 20 kg mm$^{-2}$. The pellet was annealed at 1573 K in an argon gas stream for 3–4 h. After the pulverizing, mixing, pelletizing and heating procedures had been repeated twice, the reaction product was annealed at 1273 K in a hydrogen gas stream in order to obtain the stoichiometric composition.

The X-ray diffraction study of stoichiometric $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th and La) solid solutions at room temperature was carried out using a Rigaku RAD-3C diffractometer. A NaI(Tl) scintillation counter in conjunction with a curved pyrolytic graphite monochromator was used to detect the Cu Kα radiation. Powdered specimens were loaded in a small dent (5 mm×5 mm) in a platinum sample holder without any binder. 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 ±0.05 pm.

## 3. Results and discussion

The lattice parameters of stoichiometric $(Pu_yU_{1-y})O_{2.00}$ solid solutions at room temperature measured by X-ray diffractometry are plotted versus plutonium concentration ($y$) in Fig. 1. As can be seen, the lattice parameters decrease linearly with increasing $y$. The lattice parameters obtained are in good agreement with those calculated assuming Vegard's law shown as the solid straight line in Fig. 1. The lattice parameters reported by Beauvy [2] are also shown in Fig. 1, where deviation from Vegard's law is seen at $y=0.04$ for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ solid solutions. The lattice parameters for plutonium concentrations >5 at% measured in this experiment are in good agreement with those of Beauvy [2], but the abnormal behavior observed around $y=0.04$ in that report is not seen in this experiment.

The lattice parameters of stoichiometric $(Th_yU_{1-y})O_{2.00}$ and $(La_yU_{1-y})O_{2.00}$ solid solutions at room temperature are plotted versus doped cation concentration ($y$) in Figs. 2 and 3, respectively. The results reported by Cohen and Berman [3] are also shown in Fig. 2, where abnormal behavior is observed at around 2 at% thorium concentration. However, the lattice parameters measured in this experiment increase linearly with increasing thorium concentration, reflecting Vegard's law, and no abnormal behavior is seen. It is also evident from Fig. 2 that the lattice parameters measured by Cohen and Berman are larger than those obtained in this experiment, probably due to reduction of the sample during preparation. For stoichiometric $(La_yU_{1-y})O_{2.00}$ solid solutions, the lattice parameters measured in this experiment are in good agreement with those reported by Hill et al. [4], as seen in Fig. 3. It is

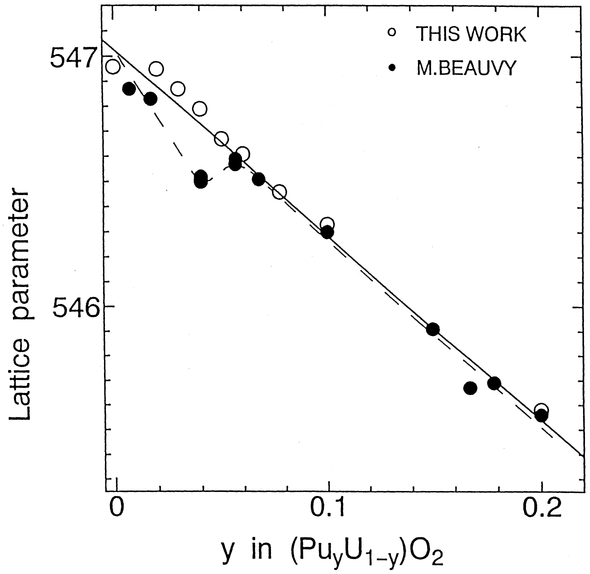

Fig. 1. Lattice parameters for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ solid solutions as a function of doped plutonium concentration at room temperature. (○) This work; (●) Beauvy [2].

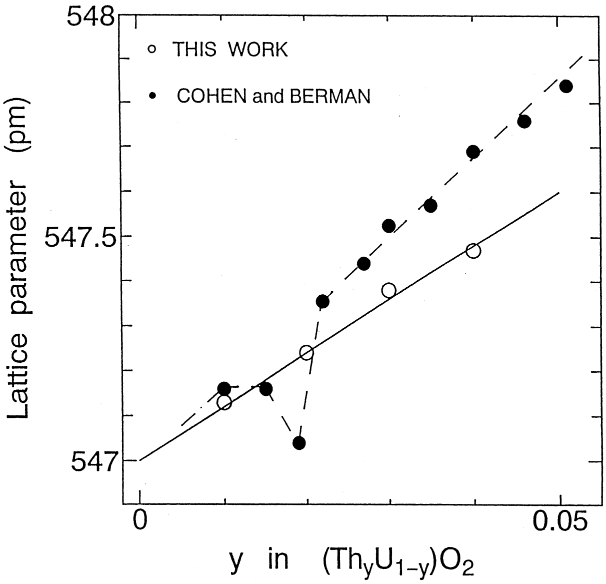

Fig. 2. Lattice parameters for stoichiometric $(Th_yU_{1-y})O_{2.00}$ solid solutions as a function of doped thorium concentration at room temperature. (○) This work; (●) Cohen and Berman [3].

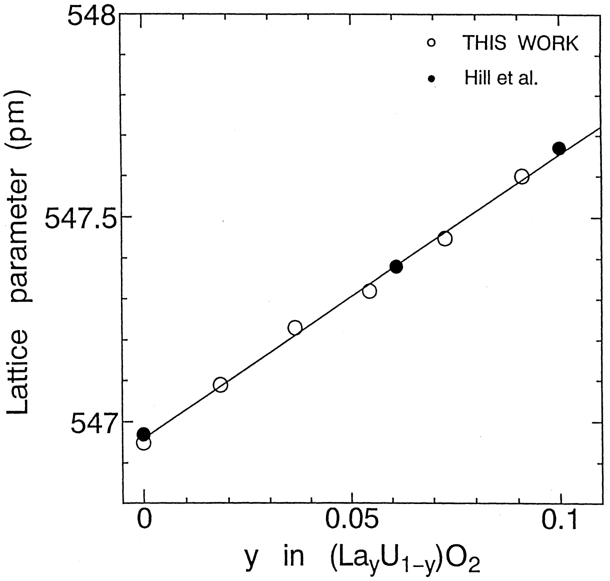

Fig. 3. Lattice parameters for stoichiometric $(La_yU_{1-y})O_{2.00}$ solid solutions as a function of doped lanthanum concentration at room temperature. (○) This work; (●) Hill et al. [4].

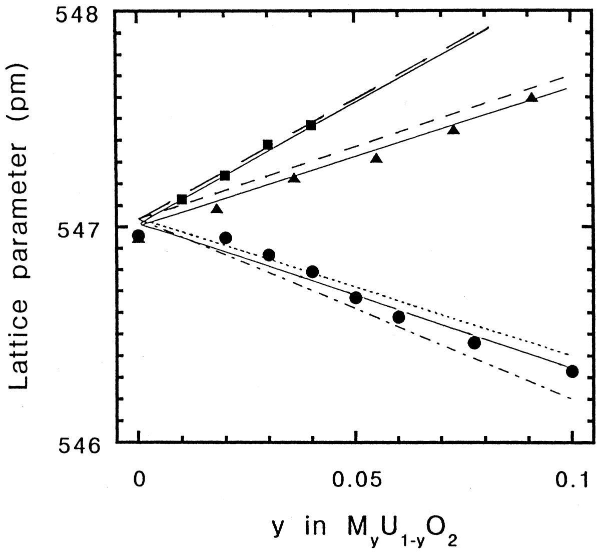

Fig. 4. Lattice parameters for stoichiometric $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th and La) solid solutions as a function of doped cation concentration at room temperature. (●) M=Pu, (■) M=Th, (▲) M=La, (– · –) M=$Pu^{4+}$, (· · ·) M=$Pu^{3+}$, (———) M=$Th^{4+}$, (- - -) M=$La^{3+}$.

also seen from Fig. 3 that the lattice parameters of $(La_yU_{1-y})O_{2.00}$ increase linearly with increasing lanthanum content.

Fig. 4 shows the relation between the lattice parameters for stoichiometric $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th and La) solid solutions at room temperature and doped content (*y*). The theoretical straight lines of *A*, discussed below, are also shown in Fig. 4. As seen in the figure, the lattice parameters for stoichiometric $(M_yU_{1-y})O_{2.00}$ (M=Pu, Th and La) solid solutions change linearly with increasing doped cation concentration, following Vegard's law, as already mentioned.

The lattice parameters (*a*) for $(M_yU_{1-y})O_{2+x}$ (M=Pu, Th and La) solid solutions are generally represented as a function of *x* and *y* as follows [5]:

$$a = C + Bx + Ay \tag{1}$$

where *A*, *B* and *C* are constants. For stoichiometric $(M_yU_{1-y})O_{2.00}$ solid solutions prepared in this experiment, *x* in Eq. (1) is considered to be zero.

If we assume that stoichiometric $(M_yU_{1-y})O_{2.00}$ solid solutions can be represented by the formula $M_y^{n+}U_{1+(n-5)y}^{4+}U_{(4-n)y}^{5+}O_2$, the mean cation radius (MCR) is given by [5]

$$\mathrm{MCR} = r(\mathrm{M}^{n+})y + 114\{1 + (n-5)y\} + 103(4-n)y \tag{2}$$

where $r(M^{n+})$ is the crystal radius of the doped cation with coordination number 8, and 114 and 103 pm are the crystal radii of $U^{4+}$ and $U^{5+}$ ions with coordination number 8 [6]. In the rigid sphere model, the contact distance is $(\sqrt{3}/4)a$ for fluorite-type crystals. Thus, the lattice constant for the fluorite-type crystal structure is

$$a = (4/\sqrt{3})\{\mathrm{MCR} + r(\mathrm{O}^{2-})\} \tag{3}$$

where $r(O^{2-})$ is the crystal radius of the $O^{2-}$ ion with coordination number 4 [5]. By substituting Eq. (2) for Eq. (3) and re-arranging, the coefficient *A* is given by

$$A = \partial a/\partial y = (4/\sqrt{3})\{r(\mathrm{M}^{n+}) + 11n - 158\} \tag{4}$$

The crystal radii of doped cations ($Pu^{4+}$, $Pu^{3+}$, $Th^{4+}$, $La^{3+}$) in $UO_2$, the theoretical value of *A* calculated from Eq. (4), and the experimental values of *A* reported in the literature and those obtained in this work are shown in Table 1. In Table 1 and Fig. 4, the observed value of *A* for doped plutonium is near the theoretical value of the +3

Table 1
Crystal radius of doped cations in $UO_2$, and the theoretical and experimental values of *A*

| Doped cation | Crystal radius (pm) | Theoretical value of *A* | Experimental value of *A* [Ref.] | Experimental value of *A* (this work) |
|---|---|---|---|---|
| $Pu^{4+}$ | 110 | −9.2 | −7.5 [7] | −7.3 |
| $Pu^{3+}$ | 122 | −6.9 | −7.5 [7] | −7.3 |
| $Th^{4+}$ | 119 | 11.5 | 16.3 [3] | 11.6 |
| $La^{3+}$ | 130 | 11.5, 6.9[a] | 7.3 [8] | 6.9 |

[a] Corrected value calculated by adding systematic deviation $-(4/\sqrt{3})\times 2$ to Eq. (4) [5].

valence rather than the +4 valence. However, if we consider that the ionic radius of $U^{4+}$ (114 pm) is close to that of $Pu^{4+}$ (110 pm) rather than $Pu^{3+}$ (122 pm) and the lattice parameters of mixed oxides decrease with increasing plutonium concentration as seen in Fig. 4, the possibility of the +4 valence is more likely. A further experiment using XPS is expected to solve this problem. The experimental value obtained in this study is in good agreement with the theoretical value for $Th^{4+}$, but is lower than the value reported by Cohen and Berman, as already mentioned. The value observed for $A$ for doped lanthanum is in good agreement with the corrected theoretical value, since Eq. (4) for +3 valence rare earth ions has to be corrected by adding the term $-(4/\sqrt{3})\times 2$ [5]. The observed value of $A$ for doped lanthanum ions obtained in this study agrees with that reported by Weitzel and Keller [8].

## 4. Conclusions

The lattice constants of stoichiometric $(M_yU_{1-y})O_{2.00}$ (M = Pu, Th and La) solid solutions at small $y$ were measured at room temperature as a function of doped cation concentration using the powder X-ray diffraction method, and the following conclusions were obtained.

(1) Deviation from Vegard's law had been reported at $y = 0.04$ for stoichiometric $(Pu_yU_{1-y})O_{2.00}$ by Beauvy and at $y = 0.02$ for stoichiometric $(Th_yU_{1-y})O_{2.00}$ by Cohen and Berman, but in this study no abnormal behavior was observed for doped cation concentrations. The lattice parameters of stoichiometric $(M_yU_{1-y})O_{2.00}$ (M = Pu, Th, La) solid solutions changed linearly with increasing doped cation at small $y$.

(2) The lattice parameters of $(La_yU_{1-y})O_{2.00}$ solid solution measured in this experiment were in good agreement with those reported by Hill et al., and no abnormal behavior was observed for the dependence of the lattice parameter on the doped lanthanum content.

(3) The valence of the doped cations was calculated from the dependence of the cation concentration on the lattice constants by assuming a random distribution of doped cations in uranium dioxide and an ionic model where every cation and anion form a rigid sphere. By comparing the theoretical values with the experimental data, plutonium, thorium and lanthanum ions in solid solution are considered to exist as $Pu^{4+}$ (or $Pu^{3+}$), $Th^{4+}$ and $La^{3+}$.

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