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# Physico-chemical properties of (U,Ce)$O_2$

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## Abstract

The high-temperature X-ray diffraction analysis of (U,Ce)$O_2$ with $CeO_2$ contents ranging from 0 to 20 mol.% $CeO_2$ was performed to obtain the variation of the linear thermal expansion coefficient with the $CeO_2$ content. Ultrasonic pulse-echo measurements were also carried out from room temperature to 673 K to estimate the change in the mechanical properties of (U,Ce)$O_2$ with the $CeO_2$ content. The variation in the linear thermal expansion coefficient at the low $CeO_2$ content region is more steep than that expected from the linear thermal expansion coefficient of $UO_2$ and $CeO_2$. The Young's and shear moduli of all (U,Ce)$O_2$ were found to decrease with rising temperature. This was due to the increase of the bond length accompanied by the thermal expansion. Although the lattice parameter decreased with $CeO_2$ content, the moduli of (U,Ce)$O_2$ were found to decrease with increasing $CeO_2$ content at room temperature. These results show that in the range from 0 to 20 mol.% of $CeO_2$, as $CeO_2$ content increases, the bottom of the potential energy in (U,Ce)$O_2$ is shallower and broader. © 1998 Elsevier Science S.A.

*Keywords:* Sound velocity; (U,Ce)$O_2$; Mechanical properties; Potential energy

## 1. Introduction

Cerium is produced in nuclear fuel as one of the fission products of high yields. The knowledge of the characteristics of (U,Ce)$O_2$ is, therefore, of basic importance for understanding the behavior of uranium dioxide fuel under irradiation 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 promising fissile material in fast breeder reactors, because of their similar chemical and/or thermodynamic behavior. In the cerium–uranium–oxygen system, as well as in the plutonium–uranium–oxgen system, it has been shown that there exists a homogeneous region of the solid solution with a fluorite structure. For (U,Ce)$O_2$, thermodynamical properties [1,2] and the lattice parameter from X-ray diffraction analysis have been determined. Such studies have revealed a similar phase diagram for (U,Ce)$O_2$ and (U,Pu)$O_2$. Therefore, the studies of the physico–chemical properties of (U,Ce)$O_2$ would contribute to our knowledge of the properties of (U,Pu)$O_2$. The strength of the mixed oxide is a very important property involving the reliability and the safety of nuclear fuel elements. As the elastic modulus is a fundamental property in understanding the strength of materials, many studies [3–7] have been performed on uranium dioxide. However, there is limited information on the influence of the microstructure on the mechanical properties of the mixed oxide.

In the present study, (U,Ce)$O_2$ has therefore been selected, and the mechanical properties and the lattice parameter were examined for (U,Ce)$O_2$ with low $CeO_2$ contents.

## 2. Experimental

### 2.1. Sample preparation

The $UO_2$ and (U,Ce)$O_2$ sample pellets used in the present study were supplied by Nuclear Fuel Industries, Ltd. The $UO_2$ and $CeO_2$ powders were mixed with a kind of organic binder and a starchy pore former (0–11.6 g, according to the porosity desired), and pressed in a steel die into a pellet of 20 mm in diameter and 10 mm in length. The binder was burned out at 1173 K for 2 h in flowing hydrogen, and the pellets were also sintered in hydrogen at 2023 K for 4 h. The compositions of (U,Ce)$O_2$ were 5, 10, 15 and 20 mol.% of $CeO_2$, and the porosities were about 6, 15, 22% for each sample. The pellet prepared without the pore former has a porosity of 6%.

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These samples appeared to be stoichiometric judging from the lattice parameter given by X-ray diffraction analysis.

### *2.2. High-temperature X-ray diffraction analysis*

The high-temperature X-ray diffraction analysis was carried out using a diffractometer from room temperature to 1273 K for $UO_2$ and 5 and 15 mol.% $CeO_2$ compounds, and the change in the linear thermal expansion coefficient with the $CeO_2$ content was estimated.

### *2.3. Ultrasonic pulse-echo measurement*

Ultrasonic pulse-echo measurement at room temperature was carried out to estimate the change in the mechanical properties of $(U,Ce)O_2$ with the $CeO_2$ content. The temperature dependence of the longitudinal sound velocity of $(U,Ce)O_2$ were also measured up to 673 K. The apparatus for the measurement of the sound velocity of $(U,Ce)O_2$ was designed and constructed similarly to those described in Ref. [8].

## 3. Results and discussion

### *3.1. The variation in the linear thermal expansion coefficient with the $CeO_2$ content*

The expansion data for $UO_2$ and $(U,Ce)O_2$ are shown in Fig. 1. The expansion data for stoichiometric $UO_2$ obtained from the lattice parameter in the present study was compared with the value derived from the Martin equation [9], and the value of the lattice parameter $L$ (=552.3 pm at 1268 K) is in good agreement with the value ($L$=551.8 pm at 1268 K) calculated from Martin equation. The experimental data for the 15-mol.% $CeO_2$ compound vary widely, and it seems that there are two domains (below and above ~800 K) for this compound. However, because there was no reason of this discontinuity, a linear interpolation of the experimental points for the 15-mol.% $CeO_2$ compound was made. In Fig. 1, the lattice parameter of the 5-mol.% $CeO_2$ compound is slightly higher than the value of $UO_2$. In our previous study [8], however, the variation in the lattice parameter of $(U,Ce)O_2$ with $CeO_2$ content closely follows the Vegard law. Because the lattice parameters of all samples except for the 5-mol.% $CeO_2$ compound are in good agreement with the previous data, the O/M ratio for the 5-mol.% $CeO_2$ compound may be slightly smaller than 2 in the present study.

The change in the linear thermal expansion coefficient $\alpha$ with the $CeO_2$ content obtained from the experimental data is shown in Fig. 2. The linear thermal expansion coefficient of $(U,Ce)O_2$ is found to decrease with increasing $CeO_2$ content. The linear thermal expansion coefficient of $UO_2$ was calculated from the reported expansion data [10], and the value of $\alpha(UO_2)=10.4\times10^{-6}\ K^{-1}$) averaged over the temperature range of 273–1273 K was estimated. The thermal expansion coefficient of $UO_2$ obtained in the present study is in good agreement with the value calculated from the reported expansion data.

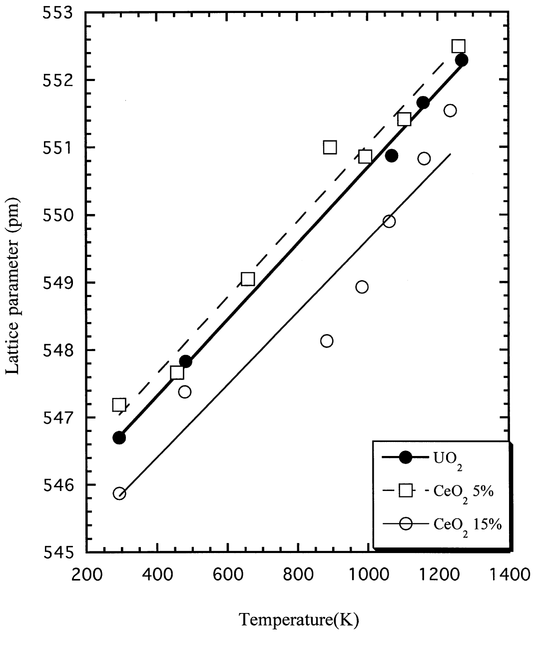

Fig. 1. Change in the lattice parameter of $(U,Ce)O_2$ with temperature.

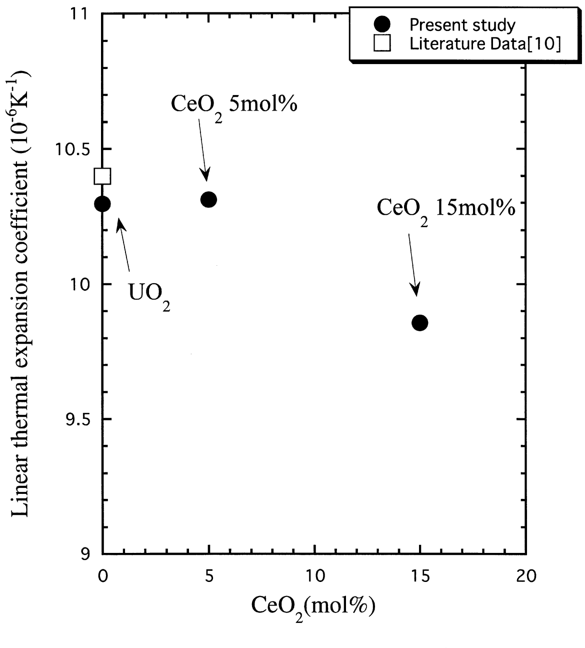

Fig. 2. Change in the linear thermal expansion coefficient of $(U,Ce)O_2$ with the $CeO_2$ content.

### 3.2. The change in the mechanical properties of $(U,Ce)O_2$ with the $CeO_2$ content from room temperature to 673 K

In our previous study [8], the shear modulus $G$ and Young's modulus $E$ of $(U,Ce)O_2$ estimated from the longitudinal velocity $V_L$ and shear sound velocity $V_S$ at room temperature were found to decrease with increasing $CeO_2$ content. And Poisson's ratio estimated from $V_S$ and $V_L$ also appeared to decrease with the $CeO_2$ content. When the Poisson's ratio increases, the deformation can occur more easily and the brittleness of materials decreases. Thus, the reduction in the Poisson's ratio yielded by the $CeO_2$ addition into $UO_2$ means that $(U,Ce)O_2$ is more brittle than $UO_2$.

The temperature dependence of the longitudinal sound velocity $V_L$ was measured up to 673 K, and the variation of $E$ and $G$ with temperature was estimated. The change in $V_L$ of $(U,Ce)O_2$ with temperature is shown in Fig. 3. As shown in this figure, the $V_L$ of all samples decrease with increasing temperature, and this means that the $E$ and $G$ of $(U,Ce)O_2$ are reduced. In the present study, as the glue joint between the sample and delay line could not be used for the shear sound velocity measurement, the change in $V_S$ with temperature could not be observed. At room temperature, fully dense $UO_2$ has a Poisson's ratio of 0.319 reported by Skelding [11] and, as the temperature increases, the Poisson's ratio increases and approaches 0.5, which is characteristic of a completely plastic substance. But, from the effect of temperature on the Young's and shear moduli reported by Marlowe [12], in the present study the variation of the Poisson's ratio with the temperature is considered to be small in the temperature range of 273–673 K. Hence, we assumed that the $V_S$ could be expressed $V_L\sqrt{\ }/3$, and estimated the $E$ and $G$.

Figs. 4 and 5 show the variations of $E$ and $G$ with temperature. The changes in the Young's and shear moduli of $(U,Ce)O_2$ with temperature were found to be smaller than the change of $UO_2$. It is consistent with the result that the linear thermal expansion coefficient of $(U,Ce)O_2$ (*RT*~ 1273 K), which derived from the high temperature X-ray diffraction analysis, decreased with increasing $CeO_2$ content.

The Young's and shear moduli of all $(U,Ce)O_2$ were found to decrease with rising temperature. In general, it is known that $E$ and $G$ of materials decrease as the temperature increases. As the elastic properties of materials have a close relation with the attractive force among the ionic atoms or constituent element, when the bond length increases with temperature due to the thermal expansion, the moduli of the material decreases with the reduction of the attractive force. At room temperature, however, although the lattice parameter decreased with $CeO_2$ content, the moduli of $(U,Ce)O_2$ were found to decrease with increasing $CeO_2$ content. This means that the potential energy in $(U,Ce)O_2$ decreases with the reduction in the bond length yielded by the $CeO_2$ addition into $UO_2$.

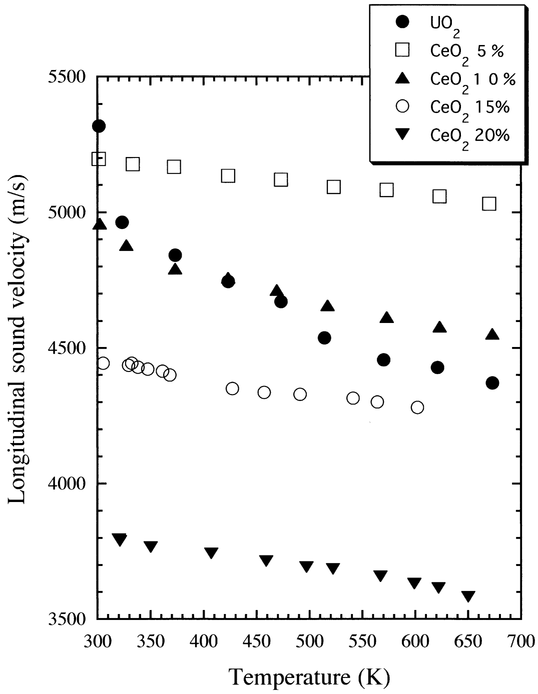

Fig. 3. Change in the longitudinal sound velocity of $(U,Ce)O_2$ with temperature.

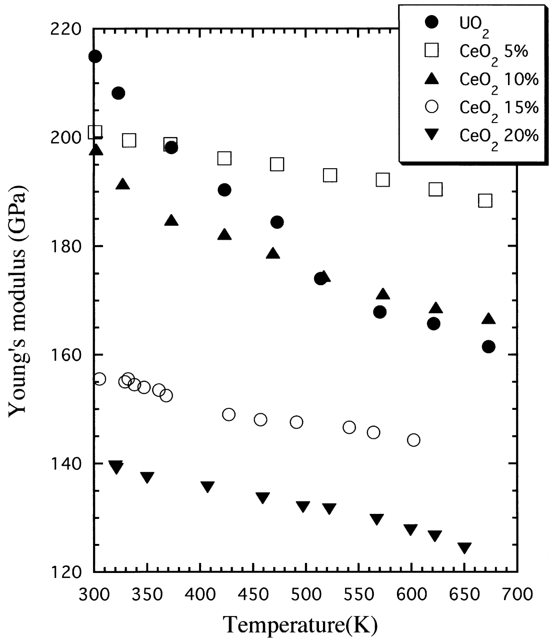

Fig. 4. Change in the Young's modulus of fully dense $(U,Ce)O_2$ with temperature.

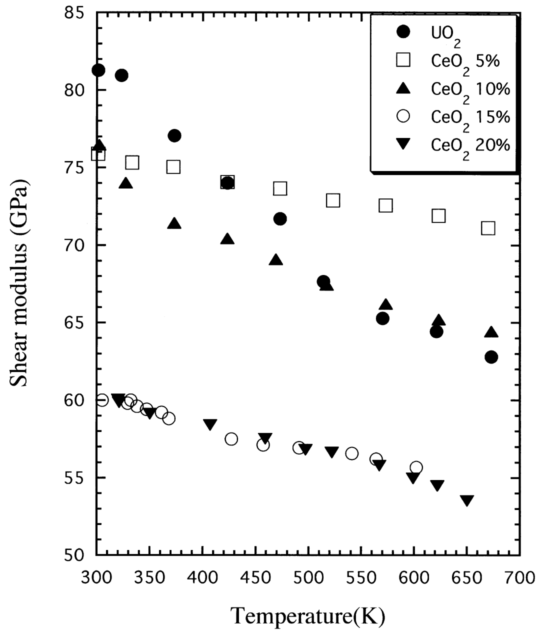

Fig. 5. Change in the shear modulus of fully dense $(U,Ce)O_2$ with temperature.

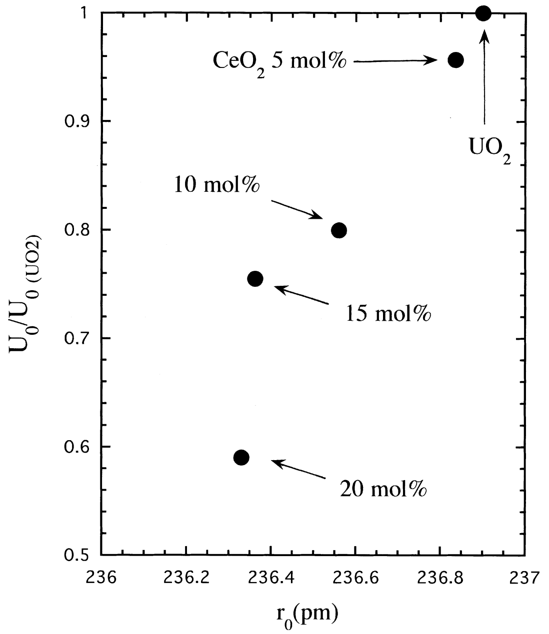

Fig. 6. Change in the relative energy of dissociation in $(U,Ce)O_2$ with $r_0$.

### 3.3. Evaluation of the change in the potential energy with the $CeO_2$ content

The Debye temperature $\Theta_D$ for $UO_2$ was estimated to be 379 K at room temperature, and decreased with increasing $CeO_2$ content [8]. This means that the bottom of the potential energy in $(U,Ce)O_2$ is broadened by the $CeO_2$ addition into $UO_2$.

In general, to determine the absolute values of the energy of dissociation in $(U,Ce)O_2$ is difficult, but the change of it can be evaluated from the Young's modulus and the atomic volume in $(U,Ce)O_2$ using following relation. The change in the potential energy with the $CeO_2$ content was evaluated by considering Morse potential as the potential energy in $(U,Ce)O_2$ [13]. Morse potential energy is defined by,

$$U = U_0[\exp\{-2c(r-r_0)\} - 2\exp\{-c(r-r_0)\}]$$

where $U_0$ is the energy of dissociation in $(U,Ce)O_2$, $r$ is the bond length, $r_0$ is the bond length at 0 K, and $c$ is the constant. The stress, required for deforming the crystals, is given by,

$$\sigma \cong -\left(\frac{\partial U}{\partial r}\right)\left(\frac{1}{r_0^2}\right)$$

The strain $\epsilon$ is given by $\mathrm{d}r/r$, thus Young's modulus $E$ is given by,

$$E = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\epsilon}\right)_{r\to r_0} \cong -\left(\frac{1}{r_0}\right)\left(\frac{\partial^2 U}{\partial r^2}\right)_{r=r_0}$$

$$= -2c^2\left(\frac{U_0}{r_0}\right) \propto \left(\frac{U_0}{\Omega}\right) \quad \left(\Omega \cong \frac{\pi r_0^3}{6}, c \cong \frac{1}{r_0}\right) \therefore U_0 \propto E \cdot \Omega$$

where $\Omega$ is the atomic volume in $(U,Ce)O_2$ estimated from the lattice parameter obtained in the previous study [8]. Thus, $U_0$ is proportional to the product of $E$ and $\Omega$. Fig. 6 shows the change in the relative energy of dissociation in $(U,Ce)O_2$ with $r$ (bond length). The energy of dissociation in $(U,Ce)O_2$ was found to be decreased with decreasing the bond length (increasing $CeO_2$ content). This is the reason of the decrease of the modulus of $(U,Ce)O_2$ when the lattice parameter decreases.

## 4. Conclusions

The high-temperature X-ray diffraction analysis and ultrasonic pulse-echo measurement of $(U,Ce)O_2$ with the $CeO_2$ contents ranging from 0 to 20 mol.% of $CeO_2$ were performed to elucidate the change of physico-chemical and mechanical properties of $UO_2$ caused by $CeO_2$ addition.

The variation in the linear thermal expansion coefficient at low $CeO_2$ content region is more steep than that expected from the linear thermal expansion coefficient of $UO_2$ and $CeO_2$. The changes in the Young's and shear moduli of $(U,Ce)O_2$ with temperature were found to be smaller than the change of $UO_2$. It is consistent with the result that the linear thermal expansion coefficient of $(U,Ce)O_2$ decreased with increasing $CeO_2$ content.

The Young's and shear moduli of all $(U,Ce)O_2$ were found to decrease with rising temperature. This was due to the increasing of the bond length accompanied by the thermal expansion. Although the lattice parameter decreased with $CeO_2$ content, the moduli of $(U,Ce)O_2$ were found to decrease with increasing $CeO_2$ content at room temperature.

These results shows that in the range from 0 to 20 mol.% of $CeO_2$, as $CeO_2$ content increases, the bottom of the potential energy in $(U,Ce)O_2$ is shallower and broader.

## References

[1] R. Ducroux, Ph.J. Baptiste, J. Nucl. Mater. 97 (1981) 333.
[2] D.I.R. Norris, P. Kay, J. Nucl. Mater. 116 (1983) 184.
[3] R. Scott, A.R. Hall, J. Williams, J. Nucl. Mater. 1 (1959) 39.
[4] J.B. Wachtman, et al., J. Nucl. Mater. 16 (1965) 39.
[5] J. Belle, B. Lustman, TID-7546.
[6] N. Igata, K. Domoto, J. Nucl. Mater. 45 (1972) 317.
[7] R.J. Forlano, A.W. Allen, R.J. Beals, J. Am. Ceram. Soc. 50 (1967) 93.
[8] K. Yamada, et al., J. Nucl. Mater 247 (1997) 289.
[9] D.G. Martin, J. Nucl. Mater 152 (1988) 94.
[10] Thermophysical properties of matter, The TPRC data series vol. 13, IFI/Plenum Data Co., New York, 1970.
[11] B.R. Skelding, AERE—Trans. 1094 (1967).
[12] M.O. Marlowe, J. Nucl. Mater. 33 (1968) 242.
[13] A. Kelly, Strong Solids, Oxford University Press, London, 1966.