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Thermodynamic and mechanical properties of $Ce_{1-x}Hf_xO_2$ ($x = 0$–0.10) solid solutions

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Abstract

Thermal expansion and mechanical properties of $Ce_{1-x}Hf_xO_2$ ($x = 0$–0.10) solid solutions were measured from 100 to 850 K by TMA and from 180 to 303 K by ultrasonic pulse methods, as a function of temperature and hafnium concentration. Using these measured values and reported specific heat capacities (C_p) at 298.15 K, Grüneisen parameters (γ) of $Ce_{1-x}Hf_xO_2$ were calculated from the thermodynamic relation $\gamma = 3\alpha VK_a/C_p$. Then heat capacities C_p of $Ce_{1-x}Hf_xO_2$ ($x = 0$–0.10) at temperatures from 150 to 800 K were calculated by using the equation $C_p = 3\alpha VK_a/\gamma$. The calculated C_p of undoped CeO_2 was in reasonable agreement with the reported value over a wide temperature range. Thus, it seems to be reasonable to derive heat capacities of $Ce_{1-x}Hf_xO_2$ solid solutions as well as CeO_2 by using this method. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Many studies on thermodynamic properties of UO_2 and $U_{0.8}Pu_{0.2}O_2$, which have been used for light water reactor and fast breeder reactor fuels, have been done, but few on other $U_{1-x}Pu_xO_2$ and $Ce_{1-x}Hf_xO_2$ solid solutions with the same valence.

We have obtained the linear thermal expansion (LTE) of the actinide solid solutions $U_{1-x}Np_xO_2$ ($x = 0$–1) and $Np_{1-x}Pu_xO_2$ ($x = 0$–1) by high-temperature X-ray diffraction analysis [1–3]. Recently, the LTE data of $Ce_{1-x}Hf_xO_2$ solid solutions having the same fluorite-type crystal structure have been measured by low- and high-temperature X-ray diffraction analysis in order to get more precise values especially around room temperature [4]. In these papers, we attempted to calculate the specific heat capacities from the thermodynamic relation, C_p (J K^{-1} mol^{-1}) = $3\alpha VK_a/\gamma$, using measured LTE coefficient data (α), measured molar volume (V) and estimated mechanical properties (K_a: adiabatic bulk modulus, γ: Grüneisen constant) [1–4].

In this study, thermal expansion and mechanical properties of $Ce_{1-x}Hf_xO_2$ ($x = 0$–0.10) solid solutions were measured by thermomechanical analysis (TMA) and ultrasonic pulse methods, respectively. Linear thermal expansion coefficients (α) calculated from sample length (L) by TMA are expected to be more accurate than those from lattice constants by X-ray diffraction analysis due to more measuring points against temperature. Mechanical properties, such as bulk modulus, can be calculated from longitudinal and transverse sonic wave velocities. From measured thermodynamic and mechanical properties, the specific heat capacity (C_p) can be derived from the thermodynamic equation $C_p = 3\alpha VK_a/\gamma$. This method permits the use of smaller samples, compared to calorimetry. We describe the derivation of heat capacity data, compare the calculated heat capacities of CeO_2 with measured values and apply this method to $Ce_{1-x}Hf_xO_2$ solid solutions.

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2. Experimental

Starting materials were high-purity CeO_2 (Kojundo Chemical Laboratory, 99.99%) and HfO_2 (Rare Metallic, 99.95%). CeO_2 and HfO_2 powders of the required proportion were mixed thoroughly in an agate mortar and pressed in a steel die to form pellets. The pellets were sintered in air at 1873 K for 40 h. All samples prepared were confirmed to be single phase by X-ray powder diffractometry at room temperature, and lattice parameters were calculated from the X-ray profile of each sample.

Thermal expansion of $Ce_{1-x}Hf_xO_2$ solid solutions (5 mm in diameter and 10 mm in thickness) was measured from 100 to 850 K in air at a heating rate of approximately 2.0 K min^{-1} and a sampling time of 1.0 s using a Rigaku Thermo Plus TMA.

The longitudinal (v_L) and transverse (v_T) sonic wave velocities of $Ce_{1-x}Hf_xO_2$ were measured in vacuum every 5 K from 180 to 303 K by an ultrasonic pulse method using Toshiba-Tungalloy UML-L equipment. Both longitudinal (v_L) and transverse (v_T) sonic wave velocities were measured at the same time with this instrument. The frequency of oscillator used was 5 MHz. The temperature was controlled to within ±0.1 K during the measurements. Adiabatic bulk modulus (K_a) and Debye temperature (θ_D) were calculated from v_L and v_T, as described below.

3. Results and discussion

The normalized lengths (L/L_0) of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05, 0.10$) solid solutions, measured by TMA method as a function of temperature, are shown in Fig. 1. Each length (L) was normalized to the reference length (L_0) at 298.15 K. All (L/L_0) values increased smoothly with increasing temperature from 100 to 850 K. This indicates that no phase transition occurred in the temperature range investigated. In Fig. 1, the (L/L_0) data increase with increasing Hf content at high temperatures and decrease at low temperatures.

The normalized lengths of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05$, 0.10) in Fig. 1 were transformed to absolute lattice parameters using a reference value at 298.15 K measured by X-ray diffraction in our previous work [4]. Fig. 2 shows these transformed lattice parameters of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05, 0.10$) solid solutions. In this figure, the original lattice parameters measured by low- and high-temperature X-ray diffraction in our previous work [4] and those compiled by Touloukian et al. [5] are also plotted. The results from this study are in good agreement with our previous values in a wide temperature range and are slightly higher than those of [5] at high temperatures. The lattice parameters of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05, 0.10$) solid solutions decrease with increasing Hf content, because the ionic radius of hafnium (97 pm) is smaller than that of cerium (111 pm) [6].

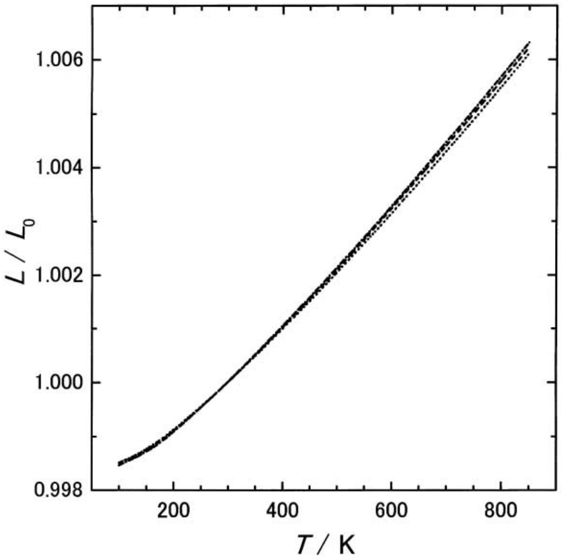

Fig. 1. Normalized length (L/L_0) of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05$ and 0.10) solid solutions as a function of temperature. (···) $x = 0$, (- - -) $x = 0.05$, (-··) $x = 0.10$.

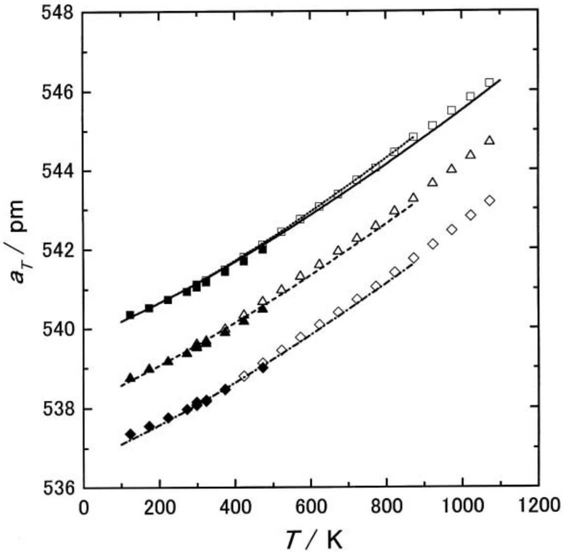

Fig. 2. Lattice parameters of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05$ and 0.10) solid solutions as a function of temperature. Dotted line (···) $x = 0$, dashed line (- - -) $x = 0.05$ and dash-dotted line (-··) $x = 0.10$ are lattice parameters transformed from TMA in this study. Lattice parameters of closed and open symbols (■, □) $x = 0$, (▲, △) $x = 0.05$ and (◆, ◇) $x = 0.10$ are measured by low- and high-temperature X-ray diffraction analysis, respectively, in our previous study [4]. Solid line is compiled by Touloukian et al. [5].

The linear thermal expansion coefficients (α) were calculated from the slopes of the plots of (L/L_0) data against temperature in Fig. 1. The slope at a certain temperature, T_1, was calculated by a least squares method from 1000 (L/L_0) data in a 20–30 K range around $T = T_1$. The (L/L_0) data in the 20–30 K range are considered to be approximately linear. By using these data, the linear thermal expansion coefficients (α) of $Ce_{1-x}Hf_xO_2$ solid solutions were calculated at temperatures from 150 to 800 K. The calculated α of $Ce_{1-x}Hf_xO_2$ $(x = 0, 0.05$ and $0.10)$ solid solutions was fitted to the following function of temperature:

$$\alpha = b_0 + b_1 T + b_2/T^2,$$

where b_0, b_1 and b_2 are constants, independent of temperature. The results obtained are shown in Fig. 3 as a function of temperature. At constant temperature, α increases with increasing Hf concentration. Larger α implies weaker bond strength of M–O $(M = Ce_{1-x}Hf_x)$ in the $Ce_{1-x}Hf_xO_2$ solid solutions.

The longitudinal (v_L) and transverse (v_T) sonic wave velocities of $Ce_{1-x}Hf_xO_2$ $(x = 0, 0.05, 0.10)$ solid solutions measured by the ultrasonic pulse method are shown in Fig. 4 as a function of temperature. The v_L and v_T at constant temperature decrease with increasing Hf content. By using both velocities, the adiabatic bulk modulus (K_a) and Debye temperature (θ_D) were calculated from the following equations:

$$K_a = \rho\{v_L^2 - (4/3)v_T^2\},$$

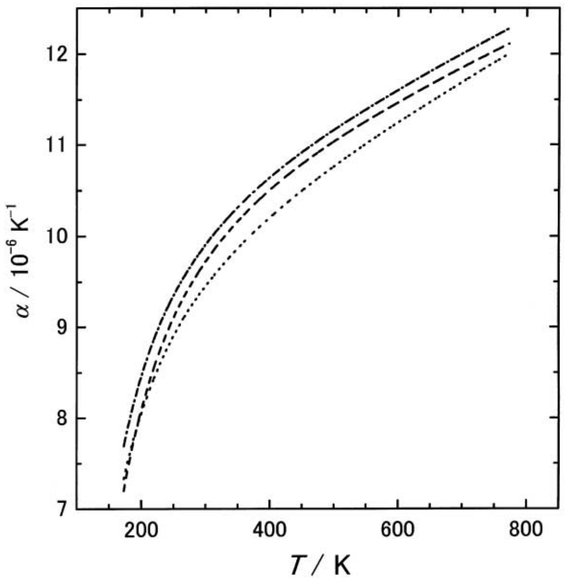

Fig. 3. Linear thermal expansion coefficients (α) of $Ce_{1-x}Hf_xO_2$ $(x = 0, 0.05$ and $0.10)$ solid solutions as a function of temperature. (···) $x = 0$, (- - -) $x = 0.05$, (-··-) $x = 0.10$.

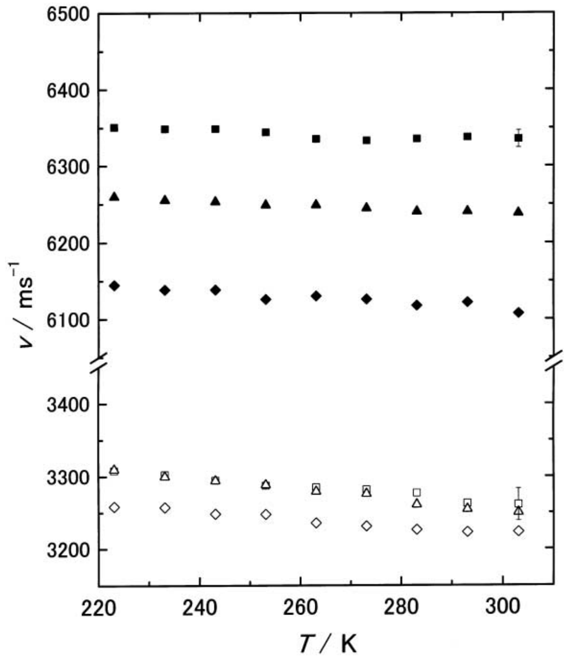

Fig. 4. Longitudinal (v_L) and transverse (v_T) sonic wave velocities of $Ce_{1-x}Hf_xO_2$ $(x = 0, 0.05$ and $0.10)$ solid solutions as a function of temperature. Closed and open symbols are longitudinal and transverse sonic wave velocities, respectively. (■, □) $x = 0$, (▲, △) $x = 0.05$, (◆, ◇) $x = 0.10$.

$$\theta_D = (h/k_B a)(3N/4\pi)^{1/3} v_m,$$

$$v_m^{-3} = (1/3)(v_L^{-3} + 2v_T^{-3}),$$

where ρ is density, h is the Planck constant, k_B is the Boltzmann constant, a is the lattice parameter and N is the number of atoms per unit cell. Figs. 5(a) and (b) show K_a and θ_D of $Ce_{1-x}Hf_xO_2 (x = 0, 0.05, 0.10)$ solid solutions as a function of temperature, respectively. The adiabatic bulk modulus shows little dependence on temperature, while the Debye temperature decreases slightly with increasing temperature. The K_a and θ_D of $Ce_{1-x}Hf_xO_2$ decrease with increasing Hf content. This is due to decreasing bond energy of M–O $(M = Ce_{1-x}Hf_x)$ in $Ce_{1-x}Hf_xO_2$ with increasing Hf content. These results also agree with larger α at higher Hf content.

The Grüneisen parameter (γ) of $Ce_{1-x}Hf_xO_2$ can be calculated from the thermodynamic relation $\gamma = 3\alpha V K_a/C_p$. To do this, V is calculated from the lattice parameters measured by X-ray diffractometry in our previous study [5]. The heat capacity C_p for $Ce_{1-x}Hf_xO_2$ solid solutions, $C_p(Ce_{1-x}Hf_xO_2)$, at 298.15 K was estimated from the Kopp–Neuman relation $C_p(Ce_{1-x}Hf_xO_2) = (1 - x)C_p(CeO_2) + xC_p(HfO_2)$, where $C_p(CeO_2)$ and $C_p(HfO_2)$ are heat capacity data of CeO_2 (61.54 J K^{-1} mol^{-1}) and HfO_2 (60.26 J K^{-1} mol^{-1}) at 298.15 K, respectively [7]. Using these values, γ of

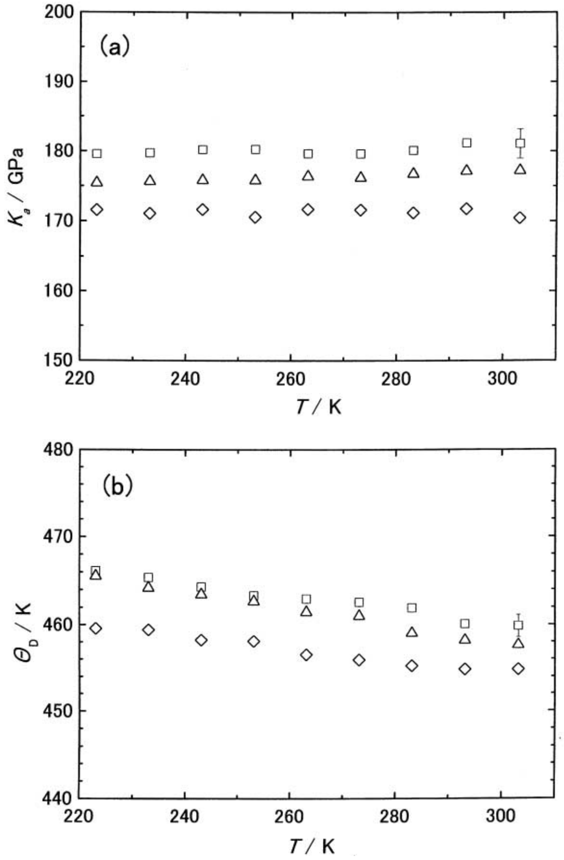

Fig. 5. Adiabatic bulk modulus (K_a) and Debye temperature (θ_D) of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05$ and 0.10) solid solutions as a function of temperature. (a) Adiabatic bulk modulus (K_a), (b) Debye temperature (θ_D). (□) $x = 0$, (△) $x = 0.05$, (◇) $x = 0.10$.

$Ce_{1-x}Hf_xO_2$ at 298.15 K was calculated to be approximately 2.0, independent of Hf content.

K_a and γ are assumed to be independent of temperature, and the K_a of $Ce_{1-x}Hf_xO_2$ solid solutions at 298.15 K in Fig. 5(a) and $\gamma = 2.0$ at 298.15 K are used in subsequent calculations. Then C_p at temperatures from 150 to 800 K was calculated from measured 3α and V by using the equation $C_p = 3\alpha VK_a/\gamma$. Fig. 6 shows the temperature dependence of the calculated C_p for undoped CeO_2, together with the compiled values of MALT 2 [7] and Touloukian et al. [8]. The calculated values in this study are in reasonable agreement with the reported ones in a wide temperature range, although the calculated values are slightly higher than the reported data at low and high temperatures. The small deviation may be caused by the assumption that the K_a and γ were independent of temperature. Thus, it seems to be reasonable to apply the above method to $Ce_{1-x}Hf_xO_2$ solid solutions. Fig. 7 shows the calculated C_p of $Ce_{1-x}Hf_xO_2$ ($x = 0.5$ and 0.10) solid solutions, together with those of undoped CeO_2 in this study.

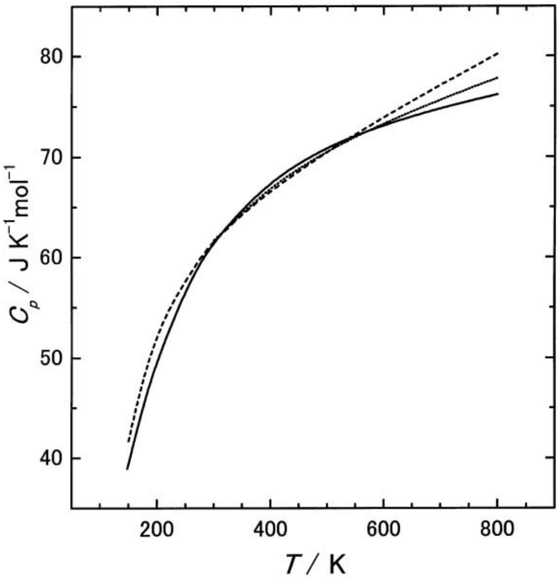

Fig. 6. Heat capacities of CeO_2 as a function of temperature. (- - -) In this study, (· · ·) by MALT 2 [7], (——) by Touloukian et al. [8].

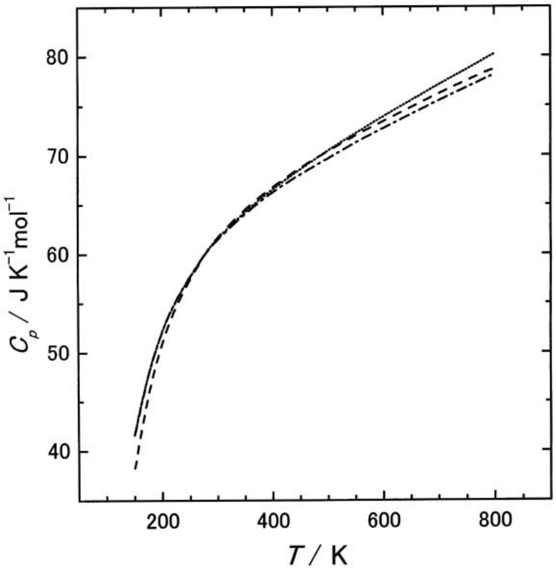

Fig. 7. Calculated heat capacities of $Ce_{1-x}Hf_xO_2$ ($x = 0, 0.05$ and 0.10) solid solutions as a function of temperature. Dotted line (· · ·) $x = 0$, dashed line (- - -) $x = 0.05$ and dash-dotted line (- · -) $x = 0.10$ are the calculated heat capacity data in this study.

4. Conclusions

Thermal expansion and mechanical properties of $Ce_{1-x}Hf_xO_2$ ($x = 0$–0.10) solid solutions were measured by TMA and ultrasonic pulse methods, and the following conclusions were obtained.

1. Thermal expansion coefficients (α) and mechanical properties (K_a, θ_D) of $Ce_{1-x}Hf_xO_2$ can be explained by the fact that bond energy between M–O ($M = Ce_{1-x}Hf_x$) decreases with increasing Hf content.
2. The heat capacities of $Ce_{1-x}Hf_xO_2$ ($x = 0$–0.10) solid solutions at temperatures from 150 to 800 K can be calculated from the measured α and V at each temperature, the measured K_a at 298.15 K and the calculated γ at 298.15 K by using the equation $C_p = 3\alpha V K_a/\gamma$.

Acknowledgements

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