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Oxygen potential measurements of fluorite-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ by EMF method

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Abstract

The dependence of the oxygen potentials ($g(O_2)$) on oxygen non-stoichiometry (y) and temperature (T) of oxygen-deficient fluorite-type (F-type) plutonium zirconate $Zr_{0.5}Pu_{0.5}O_{2-y}$ has been elucidated by electromotive force (EMF) measurements: (Pt) air $|Zr(Ca)O_{2-x}|$ $Zr_{0.5}Pu_{0.5}O_{2-y}$ (Pt). The y value of $Zr_{0.5}Pu_{0.5}O_{2-y}$ was varied at 1078 K over $0 \leqslant y < 0.10$ and the isothermal $g(O_2)$ were measured by applying the coulomb titration method. The temperature dependence of the $g(O_2)$ was also measured for each y by performing the temperature scan down to 793 K ($793 \leqslant T \leqslant 1078$ K). It was found that the $g(O_2)$ decreased from ~0 to −480 kJ/mol with increasing y from ~0 to 0.1 at 1078 K and that the isothermal $g(O_2)$ as a function of y exhibited a simple concave curve. The powder XRD results showed that $Zr_{0.5}Pu_{0.5}O_{2-y}$ maintained its single F-type structure over $0 \leqslant y < 0.10$ at 1078 K. The lattice parameters (a_0) in this system were found to increase almost linearly with y over $0 \leqslant y < 0.10$.

1. Introduction

Cubic (fluorite or pyrochlore) zirconias incorporating actinides are prominent candidate materials for various nuclear applications: targets for transmutation of actinides, inert matrix fuels and radioactive waste forms, etc., [1–4]. It is important to clarify the thermodynamic property and defect structure of these systems for such applications.

In the previous study [5], the oxygen potentials ($g(O_2)$) of pyrochlore-type (P-type) $Zr_2Pu_2O_{7+x}$, in which the Zr and Pu ions are ordered and excess oxygens (x) are incorporated into the ordered oxygen vacancy (V_O) sublattice, have been clarified. In the present study, the $g(O_2)$ of the fluorite-type (F-type) $Zr_{0.5}Pu_{0.5}O_{2-y}$ in which the Zr and Pu ions are disordered and the disordered $V_O(y)$ are introduced into the oxygen sublattice, have been investigated. Through these studies, the global feature of $g(O_2)$ of cubic zirconia with the equimolar Zr and Pu composition is to be elucidated in connection with the cation and anion ordering/disordering, in reference to the literature $g(O_2)$ data of pure F-type PuO_{2-y}.

Though the transformation of P-type $Zr_2Pu_2O_{7+x}$ to F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ have been reported in several studies [4,6], systematic comparison of the $g(O_2)$, ($g(O_2)$ as a function of oxygen non-stoichiometry (x or y) and temperature (T)) between F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ and P-type $Zr_2Pu_2O_{7+x}$ have not yet been reported.

The previous study [5] has focused on P-type $Zr_2Pu_2O_{7+x}$ and obtained the $g(O_2)$ data using electromotive force (EMF) method. The present study focuses on F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ and intends to gather its $g(O_2)$

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data over the y range ($0 \leqslant y < 0.10$) using the same EMF method. The room temperature powder XRD study was also made for the phase analysis and lattice parameter (a_0) determination of the system.

2. Experimental

2.1. Sample preparation

The F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ samples were prepared by heating P-type $Zr_2Pu_2O_{7+x}$ in air in the same way as Kulkarni et al. [6]. The P-type $Zr_2Pu_2O_{7+x}$ pellets (typically, 4 mm in diameter and 1 mm in thickness, ~100 mg in weight) were prepared by the ceramic method mentioned in the previous study [5]. The P-type $Zr_2Pu_2O_{7+x}$ pellets were heated in air at 1573 K for 6 h. Afterwards, some of the pellets were ground to powders and identified to be the single F-type phase by the XRD method (RAD-2X, Regaku Denki Co. Ltd., Japan).

2.2. Oxygen potential measurements by EMF method

The same double compartment-type EMF cell as used in the previous study [5] on the P-type $Zr_2Pu_2O_{7+x}$ was employed in the present study: Pt/O_2 in dry air/Stabilized $Zr(Ca)O_{2-x}$/F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$/Pt. The detail has been already described in [5].

Also as described there, the values of oxygen non-stoichiometry (y) were controlled and determined by the coulomb titration of oxide ions at 1078 K through the zirconia-electrolyte tube by using reference dry air gas as a source or sink of oxygen, in combination with the weight change measurements mentioned below.

In order to obtain the temperature (T) dependence of the $g(O_2)$ for a given y, temperature-scan was also made between 793 and 1078 K in both increasing and decreasing T directions.

The $g(O_2)$ of the sample were calculated from the EMF values by using the thermodynamic relation: $g(O_2) = 4EF + RT\ln P_{O_2}(\text{air})$, where E is the EMF value of the cell in volt, F is the Faraday constant, R is the gas constant, T is the temperature in Kelvin and $P_{O_2}(\text{air})$ is the oxygen partial pressure (0.206 atom) of air.

The $g(O_2)$ and temperatures in the present study are within the electrolytic domain of the zirconia sensor according to Patterson [7]. We determined the $g(O_2)$ of CeO_{2-y} by using the same cell in the previous study [5], to check the accuracy of the $g(O_2)$ data. In fact, the $g(O_2)$ data in the previous study [5] agreed with the well-accepted literature data [8] within the maximum error of 2 kJ/mol. Thus, the $g(O_2)$ data of F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ in the present study is supposed to be accurate within the maximum error of 2 kJ/mol.

2.3. Phase analysis of F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ by XRD method and weight change measurements by oxidation

The F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ samples with measured $g(O_2)$ at 1078 K were cooled to room temperature within several hours. Then, some samples were ground into powders and analyzed by XRD method to check whether the sample maintained the F-type structure and also to determine its lattice parameter. The other samples were weighed and oxidized for 6 h at 1078 K in air and thereafter again weighed by using the electrobalance (precision: ±0.02 mg, AE240, Mettler–Toledo GmbH). The oxidized samples were heated for 6 h at 1078 K in air again in order to check whether the period of 6 h is enough for complete oxidation. The y' value of $Zr_{0.5}Pu_{0.5}O_{2-y'}$ before oxidation was calculated from the following equation, assuming $y' = 0$ for the air-oxidized sample:

$$y' = (W_1 - W_0)/W_1 \cdot (M_W(Zr_{0.5}Pu_{0.5}O_2)/M_W(O)). \quad (1)$$

In Eq. (1), W_0 and W_1 are the sample weights before and after the heating (oxidation) at 1078 K in air, respectively, $M_W(Zr_{0.5}Pu_{0.5}O_2)$ is the molecular weights of $Zr_{0.5}Pu_{0.5}O_2$ ($y = 0$), and $M_W(O)$ is the atomic weights of oxygen: $M_W(Zr_{0.5}Pu_{0.5}O_2) = 197.11$, $M_W(O) = 15.9994$.

3. Results and discussion

Fig. 1 shows the result of the coulomb titration at 1078 K obtained in the present study. Table 1 summarizes the results of the weight change measurements. The y values were relatively determined by the coulomb titration alone. So the y values of the coulomb titration curve were set to minimize the standard deviation of the

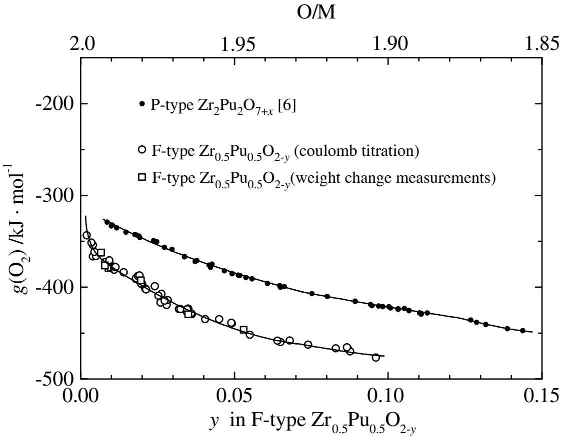

Fig. 1. The $g(O_2)$ vs. y relation at 1078 K of F-type $Pu_{0.5}Zr_{0.5}O_{2-y}$. The sign O/M stands for the molar ratio of oxygen to metal: $O/M = 2 - y = (7 + x)/4$.

Table 1
Summary on the oxygen non-stoichiometry (y' and y) data of weight change and EMF measurements

Sample number $g(O_2)$ at 1078 K (kJ/mol)	Weight (mg) before oxidation	Weight (mg) after oxidation	Weight change (mg)	y': from weight change (Eq. (1))	y: from titration curve (Fig. 1)
(1) −446.481	80.85	81.20	0.35	0.053	0.050
(2) −429.535	84.36	84.60	0.24	0.035	0.036
(3) −392.518	125.60	125.80	0.20	0.020	0.018
(4) −379.433	81.34	81.40	0.06	0.009	0.011
(5) −376.383	78.39	78.44	0.05	0.008	0.0085
(6) −362.410	112.41	112.47	0.06	0.007	0.006
(7) (∼0)	140.80	140.80	0.00	0.000	(∼0)

y values (y') from the weight change measurements and those (y) from the coulomb titration.

The $g(O_2)$ changed from ∼0 to −480 kJ/mol as y increases from ∼0 to 0.10. The $g(O_2)$ vs. y relations exhibited a single concave curve at 1078 K, suggesting no significant change in oxygen incorporation. The $g(O_2)$ data of P-type $Zr_2Pu_2O_{7+x}$ in the previous study [5] are also shown for comparison in Fig. 1. The $g(O_2)$ of F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ were lower than those of P-type $Zr_2Pu_2O_{7+x}$ by 50–70 kJ/mol at the same O/M values. This result reveals that the molar ratio of Pu^{3+} ions to Pu^{4+} ions is larger in P-type $Zr_2Pu_2O_{7+x}$ than in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ all over our measured $g(O_2)$ range; Pu^{3+} ion is more stabilized in P-type $Zr_2Pu_2O_{7+x}$ than in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$.

Fig. 2 shows the whole set of $g(O_2)$ vs. T plots obtained for F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$. The y values of respective runs were evaluated from their $g(O_2)$ at 1078 K in reference to the coulomb titration curve at 1078 K shown in Fig. 1. The literature $g(O_2)$ data of PuO_{2-y} [9] are also shown for comparison in Fig. 2. The $g(O_2)$ of F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ were higher than those of F-type $PuO_{2-y}$by 150–180 kJ/mol at the same O/M values between 793 and 1078 K (see O/M = 1.92, 1.96 in Fig. 2). This result reveals that the molar ratio of Pu^{3+} ions to Pu^{4+} ions is larger in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ than in F-type PuO_{2-y} all over our measured $g(O_2)$ and temperature ranges; Pu^{3+} ion is more stabilized in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ than in F-type PuO_{2-y}.

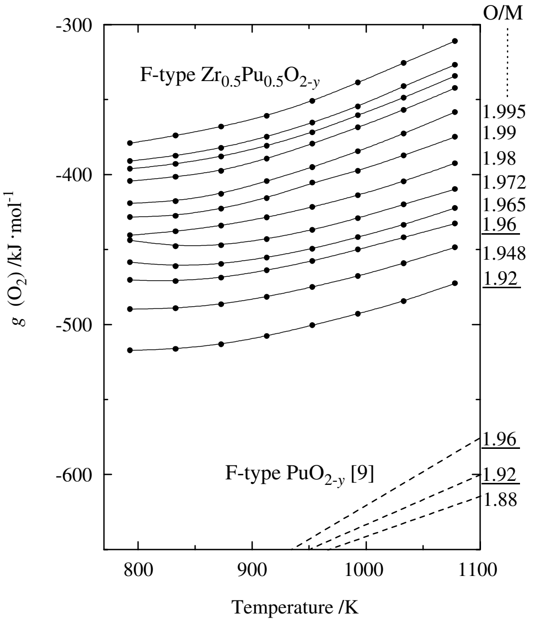

Fig. 2. Temperature dependence of the $g(O_2)$ of F-type $Pu_{0.5}$-$Zr_{0.5}O_{2-y}$.

This result is consistent with the fact that the zirconium tends to enhance the reduction of Ce^{4+} ions in cerium zirconate [2]. This tendency may be ascribed to the possibility that P-type micro ordering is partially formed in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ structure; the Zr^{4+} radius (0.084 nm) is much smaller than Pu^{4+} radius (0.096 nm) at coordination number of 8 [10]. V_O may prefer to be adjacent to Zr^{4+} ions rather than $Pu^{3,4+}$ ions, that is similar to the case of gadolinium zirconate [11], and consequently Pu^{3+} ions may be more stabilized in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ with the partial P-type ordering than in pure F-type $PuO_{2-y}$with no P-type ordering. This possibility also explains that the $g(O_2)$ of P-type $Zr_2Pu_2O_{7+x}$ with the perfect P-type ordering are higher than those of F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ with the partial P-type ordering at the same O/M values. However, to prove this possibility, more detailed structural study is needed.

The XRD patterns did not change except for their lattice parameters. All the samples were identified as single F-type phases (space group Fm-3m). This result reveals that the long-range (macro) P-type ordering of the cations (Zr and Pu) in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ did not occur at 1078 K over the measured $g(O_2)$ range. If such ordering occurred, the XRD pattern of the sample should have shown that of alternative phase, the precursor P-type $Zr_2Pu_2O_{7+x}$. However, the short-range (micro) structure could not be known by powder XRD analysis of the present study.

In Fig. 3, the lattice parameter (a_0) vs. y relation of the F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ samples derived from the

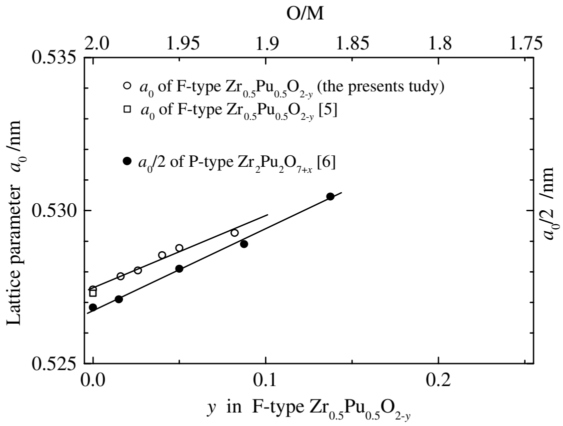

Fig. 3. Plots of the lattice parameter (a_0) vs. y plots of F-type $Pu_{0.5}Zr_{0.5}O_{2-y}$.

XRD analysis is shown. The y value of each sample is deduced from Fig. 1. The $a_0/2$ data of P-type $Zr_2Pu_2O_{7+x}$ are also shown for comparison in Fig. 3. The a_0 value (=0.5274 nm) of F-type $Zr_{0.5}Pu_{0.5}O_2$ ($O/M = 2$, $y = 0$) in the present study agrees with that (=0.5273 nm) reported by Kulkarni et al. [6]. The a_0 values were found to increase almost linearly with y over $0 \leqslant y < 0.10$. Oxygen removal from the anion sublattice changes Pu^{4+} ions to Pu^{3+} ions (ionic radii $Pu^{4+} < Pu^{3+}$). This accounts for the result. It is to be noted that the $a_0/2$ value (=0.5268 nm) of P-type $Zr_2Pu_2O_8$ ($O/M = 2$, $x = 1$) in the previous study [5] was different from the a_0 value (=0.5274 nm) of F-type $Zr_{0.5}Pu_{0.5}O_2$ ($O/M = 2$, $y = 0$). The dependence of a_0 on O/M in F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ was different from that of $a_0/2$ in P-type $Zr_2Pu_2O_{7+x}$. This result may be ascribed to the difference of the anion sublattice structure between oxygen-deficient fluorite and oxygen-excess pyrochlore.

In the present study, XRD analyses and weight change measurements of the samples were conducted within 24 h after the sample pellets were cooled to the room temperature. Therefore, the measurements were supposed to be performed without the effects of self-irradiation damage. The temperature 1078 K at which the coulomb titration was performed is above the temperature 1073 K at which the complete recovery from self-irradiation damage is achieved in the thermal conductivity of PuO_2. [12] Therefore, it is inferred that the self-irradiation damage had little effects on the $g(O_2)$ data in the present study.

4. Conclusion

In the present study, the $g(O_2)$ of oxygen-deficient F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ ($0 \leqslant y < 0.10$) was investigated by EMF method with zirconia sensor between 793 and 1078 K. The $g(O_2)$ of F-type $Zr_{0.5}Pu_{0.5}O_{2-y}$ were lower than those of oxygen-excess P-type $Zr_2Pu_2O_{7+x}$ by 50–70 kJ/mol and higher than those of pure F-type PuO_{2-y} by 150–180 kJ/mol at the same O/M values. The $g(O_2)$ of these materials depended on not only the cation composition ratio (Zr/Pu), but also the cation and anion ordering/disordering. The dependence of lattice parameters a_0 (or $a_0/2$) on O/M was found to be different between oxygen-deficient fluorite and oxygen-excess pyrochlore.

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