



## Oxygen potential of hypo-stoichiometric Lu-doped $\text{UO}_2$

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### ABSTRACT

Oxygen potentials of hypo-stoichiometric Lu-doped  $\text{UO}_2$ ,  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$ , were experimentally investigated by thermogravimetric analysis using  $\text{H}_2\text{O}/\text{H}_2$  gas equilibria at 1173, 1273 and 1473 K. The oxygen potentials of  $(\text{U,Lu})\text{O}_{2-x}$  were higher than those of other forms of rare earth-doped  $\text{UO}_2$ , specifically  $(\text{U,Nd})\text{O}_{2-x}$ ,  $(\text{U,Gd})\text{O}_{2-x}$ , and  $(\text{U,Er})\text{O}_{2-x}$ . Slope analyses for plots of oxygen potential versus deviation from stoichiometry indicated that  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  had a similar defect structure to that of the other forms of rare earth-doped  $\text{UO}_2$ . A relationship between the effective ionic radii and oxygen potentials was found for the hypo-stoichiometric rare earth-doped  $\text{UO}_2$ .

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### 1. Introduction

Rare earth-doped  $\text{UO}_2$  (RDU) attracts much attention from both technological and scientific viewpoints in the field of nuclear fuel. Various rare earth (RE) elements are generated as representative fission products (FPs) during nuclear reactor operation, which results in formation of a multi-elemental system with a continuous compositional change in nuclear fuel systems. Even in such a complicated system, chemical equilibria in nuclear fuel systems should be known in order to evaluate nuclear fuel behaviors for safe and effective reactor operation. Since oxygen potential dominates the chemical equilibria of oxide nuclear fuel systems, it should be accurately determined as a function of composition, temperature and oxygen non-stoichiometry. Oxygen potential,  $\Delta\bar{G}_{\text{O}_2}$ , is expressed as the following relationship:  $\Delta\bar{G}_{\text{O}_2} = RT \ln p_{\text{O}_2}$ , where  $R$  is the gas constant,  $T$  is temperature and  $p_{\text{O}_2}$  is equilibrium oxygen partial pressure, which is derived from the ratio of oxygen partial pressure to its standard state of 0.101 MPa. Construction of a database for  $\Delta\bar{G}_{\text{O}_2}$  of various forms of RDU is, thus, a very important task.

Numerous studies [1–6] have examined  $\Delta\bar{G}_{\text{O}_2}$  of various forms of hypo-stoichiometric RDU. Lindemer and Brynstad [7] reviewed  $\Delta\bar{G}_{\text{O}_2}$  of various forms of RDU. They mentioned that there were no significant differences in  $\Delta\bar{G}_{\text{O}_2}$  from one RDU to another, if RE-dopant has single valency of trivalent; e.g.  $\Delta\bar{G}_{\text{O}_2}$  are almost the same for Nd- [1] and Gd-doped  $\text{UO}_2$  [2], provided that their RE contents are the same. However, notable differences in  $\Delta\bar{G}_{\text{O}_2}$  have sometimes been observed among several forms of RDU with different dopants, especially in the hypo-stoichiometric region, in contrast to their finding. Oxygen potentials of La-doped  $\text{UO}_2$  [3] are much

higher than those of the other forms of RDU. Kim et al. [4] reported notably higher  $\Delta\bar{G}_{\text{O}_2}$  values of hypo-stoichiometric Er-doped  $\text{UO}_2$  than those of Nd- [1] or Gd-doped  $\text{UO}_2$  [2].

Presently, low-decontaminated fuel (LDF) doped with minor actinides (MAs) is being developed as the most promising fuel for a future fast reactor [8]. The LDF contains several percent of both MAs and FPs in its fresh fuel form. In particular, fractions of higher-mass RE elements such as Sm and Gd are larger than those in the standard burnup fuel. A higher fraction of Y is also of note. In addition, the fraction of RE-FPs in a burnup LDF become much higher than that in the standard burnup fuel owing to the extremely high burnup design specification, 250 GWD/t at the maximum. In this context,  $\Delta\bar{G}_{\text{O}_2}$  of various forms of hypo-stoichiometric RDU doped with various RE elements should be accurately determined, not only for the representative elements such as La and Nd, but also Y, Sm, and Dy. Such studies can also contribute to interpretation of fundamental aspects of oxygen hypo-stoichiometry in dioxides having a fluorite-type structure such as  $\text{CeO}_2$ - [9–13] or  $\text{PuO}_2$ -based [14] oxides, since effects of RE-dopants on  $\Delta\bar{G}_{\text{O}_2}$  are also significant for them.

In this study,  $\Delta\bar{G}_{\text{O}_2}$  of 20% Lu-doped  $\text{UO}_2$ ,  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$ , were experimentally investigated as a function of non-stoichiometry at 1173, 1273 and 1473 K by thermogravimetric analysis (TGA) with  $\text{H}_2\text{O}/\text{H}_2$  gas equilibria. No data have been reported so far for  $\Delta\bar{G}_{\text{O}_2}$  of Lu-doped  $\text{UO}_2$ . Although the Lu fraction in the LDF is rather small, Lu is of interest because it has the smallest ionic radius among all RE elements [15]. Since the final goal of this study is to elucidate a relationship between  $\Delta\bar{G}_{\text{O}_2}$  and the effective ionic radii in order to construct a practical prediction model for  $\Delta\bar{G}_{\text{O}_2}$  of burnup LDF, Lu is an appropriate choice as a representative RE element having a small ionic radius. Results were compared with other forms of RDU and were discussed from thermodynamic viewpoint.

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## 2. Experimental

Lutetium-doped  $\text{UO}_2$  solid solution sample was prepared by a conventional powder metallurgical route. Appropriate amounts of  $\text{UO}_2$  and  $\text{Lu}_2\text{O}_3$  powders were weighed and thoroughly mixed in an agate mortar with a pestle in acetone medium. The  $\text{UO}_2$  powder was derived from an ammonium diuranate precursor. The  $\text{Lu}_2\text{O}_3$  powder was from Chempur Feinchemikalien and Forschungsbedarf GmbH (99.9% purity). The mixed powder was then compacted into a columnar pellet by a uni-axial pressing unit at 200 MPa. The compacted pellet was heated at 1623 K for 4 h under He atmosphere. The heat-treated pellet was ground, thoroughly mixed and milled again. This sample preparation procedure was repeated three times in order to form a complete solid solution. Temperatures and heating times for the second and third heat-treatments were changed to 1673 K, 4.5 h and 1873 K, 4.5 h, respectively. The heating was carried out under He above 1673 K and under He containing 0.5%  $\text{H}_2$  below 1673 K. This was intended to prevent any phase changes in  $(\text{U,Lu})\text{O}_{2-x}$  during heat-treatments. X-ray diffraction analysis of the final heat-treated sample showed formation of a single phase solid solution with a fluorite-type structure,  $(\text{U,Lu})\text{O}_{2-x}$ .

About 150 mg of sample was subjected to TGA for the determination of oxygen-to-metal ratio (O/M ratio, which corresponds to  $2.00 - x$ ), as a function of  $p_{\text{O}_2}$  at pre-determined temperatures, specifically 1173, 1273 and 1473 K. A Rigaku TGA apparatus (model TG-8120) connected with a gas supply system was used. The  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  sample was loaded into an alumina pan and placed in the TGA apparatus. For reference, an alpha-alumina sample was loaded into another alumina pan and also placed in the apparatus. Equilibrium oxygen partial pressure was adjusted in the range from  $10^{-22}$  to  $10^{-10}$  MPa at 1173 K, from  $10^{-20}$  to  $10^{-9}$  MPa at 1273 K and from  $10^{-18}$  to  $10^{-5}$  MPa at 1473 K by changing the ratio of  $\text{H}_2\text{O}$  to  $\text{H}_2$  in the flowing gas. Equilibrium oxygen partial pressure was measured with a stabilized zirconia oxygen sensor. The oxygen sensor was calibrated prior to the TGA using the oxidation reaction of pure chromium metal and a standard gas containing a known amount of oxygen. Microgram order weight changes in the sample were continuously monitored while changing the  $p_{\text{O}_2}$  at the pre-determined temperatures step by step. Oxygen-to-metal ratios at various  $p_{\text{O}_2}$  at the pre-determined temperatures were calculated from the weight changes relative to the stoichiometry, O/M = 2.00. Oxygen potentials that give the stoichiometry at each temperature were defined as those showing steep increases with increase of O/M ratio. This definition is appropriate considering the similarity between the Lu–U–O system and other RE–U–O systems [16] which show the steep increase of  $\Delta\bar{G}_{\text{O}_2}$  at the stoichiometry.

## 3. Results and discussion

Fig. 1 shows relationships between O/M ratio and  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  at 1173, 1273 and 1473 K. At all temperatures,  $\Delta\bar{G}_{\text{O}_2}$  increases with increase of O/M ratio. Furthermore, at each temperature, a particularly steep increase of  $\Delta\bar{G}_{\text{O}_2}$  appears, which is the  $\Delta\bar{G}_{\text{O}_2}$  that gives the stoichiometry, O/M = 2.00, according to the definition made in the previous section. This tendency is, as shown later, the same as that seen for other forms of RDU, which indicates the complete similarity of  $\Delta\bar{G}_{\text{O}_2}$  isotherms for Lu-doped and other forms of RDU. At about O/M = 1.98,  $\Delta\bar{G}_{\text{O}_2}$  was about 40 kJ/mol larger at 1473 K than at 1273 K, which was 30 kJ/mol larger than at 1173 K. This relationship for  $\Delta\bar{G}_{\text{O}_2}$  values is also seen at O/M = 1.99.

The above mentioned results are compared with those of other forms of RDU to elucidate effects of Lu-doping to  $\text{UO}_2$  on  $\Delta\bar{G}_{\text{O}_2}$ . A

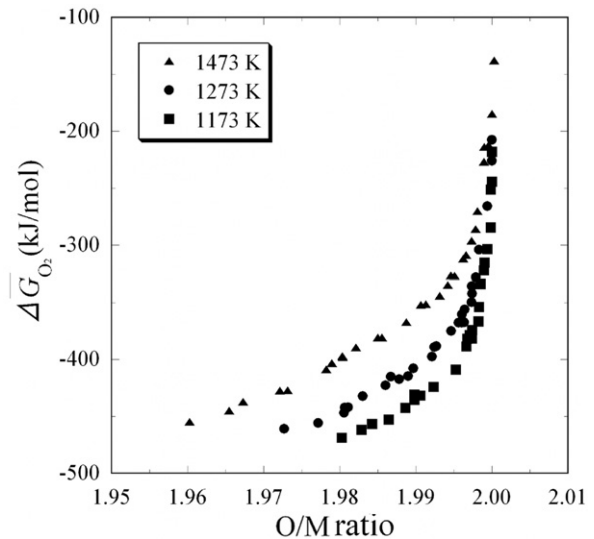


Fig. 1. Oxygen potentials of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  as a function of non-stoichiometry at 1173, 1273 and 1473 K.

consideration based on defect structure in the RDU is also carried out for this purpose.

Comparisons of  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  with those of  $(\text{U,Gd})\text{O}_{2-x}$  [2,5] and  $(\text{U,Er})\text{O}_{2-x}$  [4] having comparable RE-dopant contents are shown in Fig. 2(a) and (b) at 1273 and 1473 K, respectively. The  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U,Nd})\text{O}_{2-x}$  [1] were not plotted on the graphs since their values are almost the same as those of  $(\text{U,Gd})\text{O}_{2-x}$  [2]. The  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  at 1273 K are higher than those of  $(\text{U}_{0.80}\text{Gd}_{0.20})\text{O}_{2-x}$  [5] and are comparable with those of  $(\text{U}_{0.73}\text{Gd}_{0.27})\text{O}_{2-x}$  [2]. From this fact, it is revealed that Lu has a larger effect on increase in  $\Delta\bar{G}_{\text{O}_2}$  of the hypo-stoichiometric RDU at a constant O/M ratio than Gd or Nd has, considering the general tendency of higher  $\Delta\bar{G}_{\text{O}_2}$  with a larger RE-dopant content. The above mentioned relationship can also be seen in comparing with the Er-doping effect at 1473 K, as shown in Fig. 2(b). Namely, the  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  are higher than those of  $(\text{U}_{0.80}\text{Er}_{0.20})\text{O}_{2-x}$  [4]. Although the  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  are comparable with those of  $(\text{U}_{0.70}\text{Gd}_{0.30})\text{O}_{2-x}$  [5] above O/M = 1.985, it is of note that  $\Delta\bar{G}_{\text{O}_2}$  of  $(\text{U}_{0.70}\text{Gd}_{0.30})\text{O}_{2-x}$  become higher than those of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  below O/M = 1.985.

Fig. 3 shows relationships between  $p_{\text{O}_2}$  and deviation from stoichiometry,  $x$ , for  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  at each temperature. Slope  $n$  of  $\log p_{\text{O}_2}$  versus  $-\log x$  is an indicator of the predominant defect structure for non-stoichiometric oxide. Namely, what kind of defect structure is predominant in a specific O/M region can be predicted from the slope [17]. It is seen that  $n$  is about 5 for the presently measured  $x$  region at all temperatures. Slope values of  $(\text{U,Gd})\text{O}_{2-x}$  derived by two different groups are shown in Table 1. The same value  $n = 5$  as that of  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  was derived for  $(\text{U}_{0.86}\text{Gd}_{0.14})\text{O}_{2-x}$  at 1273 K and  $(\text{U}_{0.80}\text{Gd}_{0.20})\text{O}_{2-x}$  at 1273 K by Une and Oguma [2] and Lindemer and Sutton [5], respectively. Une and Oguma assigned a charged defect cluster expressed as  $(\text{V}_\text{O}\text{V}_\text{O})^{\bullet\bullet}$  with four liberated electrons for interpretation of the slope  $n = 5$  observed for  $(\text{U,Gd})\text{O}_{2-x}$ . It is seen in Table 1 that slope  $n$  decreases with increase of both Gd content and temperature for  $(\text{U,Gd})\text{O}_{2-x}$ . Nevertheless, slopes of  $(\text{U,Gd})\text{O}_{2-x}$  having 0.14–0.30 Gd content are in a narrow range, from 4 to 5 below 1473 K as shown in Table 1. Although only one slope value  $n$  of about 5 was observed for the present  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  regardless of temperatures, it is considered that  $(\text{U}_{0.80}\text{Lu}_{0.20})\text{O}_{2-x}$  has a similar type of defect structure, probably a cluster-type, as that in  $(\text{U,Gd})\text{O}_{2-x}$  in the temperature range from 1173 to 1473 K, considering the

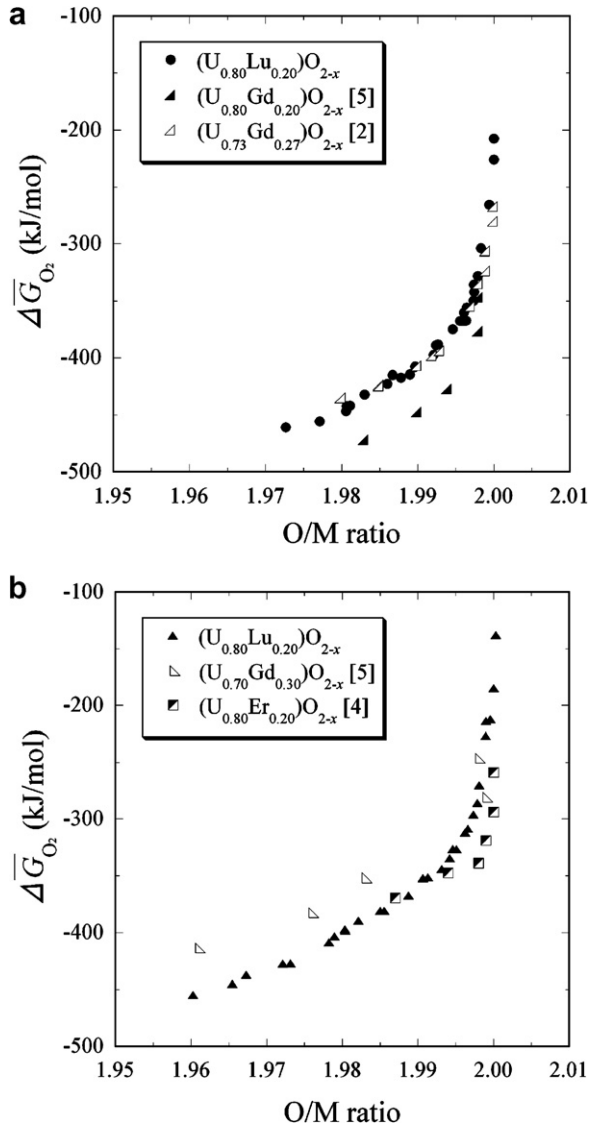


Fig. 2. Comparison of oxygen potentials of  $(U_{0.80}Lu_{0.20})O_{2-x}$  with those of  $(U,Gd)O_{2-x}$  and  $(U,Er)O_{2-x}$  at (a) 1273 K and (b) 1473 K.

similar slopes of the plots for  $(U_{0.80}Lu_{0.20})O_{2-x}$  and  $(U,Gd)O_{2-x}$ , in addition to the close similarity between Lu–U–O and Gd–U–O systems.

Figs. 4 and 5 show partial molar entropy,  $\Delta\bar{S}_{O_2}$ , and enthalpy,  $\Delta\bar{H}_{O_2}$ , of oxygen for  $(U_{0.80}Lu_{0.20})O_{2-x}$ , respectively, as a function of O/M ratio. The  $\Delta\bar{S}_{O_2}$  and  $\Delta\bar{H}_{O_2}$  were calculated by using the following thermodynamic relationships:

$$\Delta\bar{H}_{O_2} = \Delta\bar{G}_{O_2} + T\Delta\bar{S}_{O_2}, \quad (1)$$

$$\Delta\bar{S}_{O_2} = -\frac{\partial\Delta\bar{G}_{O_2}}{\partial T}. \quad (2)$$

The  $\Delta\bar{G}_{O_2}$  values used in these calculations were taken from those calculated from fitting isotherms as shown in Fig. 3. Both  $\Delta\bar{S}_{O_2}$  and  $\Delta\bar{H}_{O_2}$  for  $(U_{0.80}Lu_{0.20})O_{2-x}$  decrease with increase of O/M ratio. The  $\Delta\bar{S}_{O_2}$  and  $\Delta\bar{H}_{O_2}$  for all forms of RDU show steep changes, or a sign of the steep change for  $(U,Nd)O_{2-x}$ , as the O/M ratio approaches 2.00, which indicates a fundamental change of defect structure from oxygen vacancy-based to oxygen interstitial-based defects, like seen for other  $UO_2$ -based non-stoichiometric oxides. Different trends in the profiles of  $\Delta\bar{H}_{O_2}$  near stoichiometry are observed between  $(U_{0.80}Lu_{0.20})O_{2-x}$  and  $(U,Gd)O_{2-x}$  or  $(U,Nd)O_{2-x}$ , i.e.

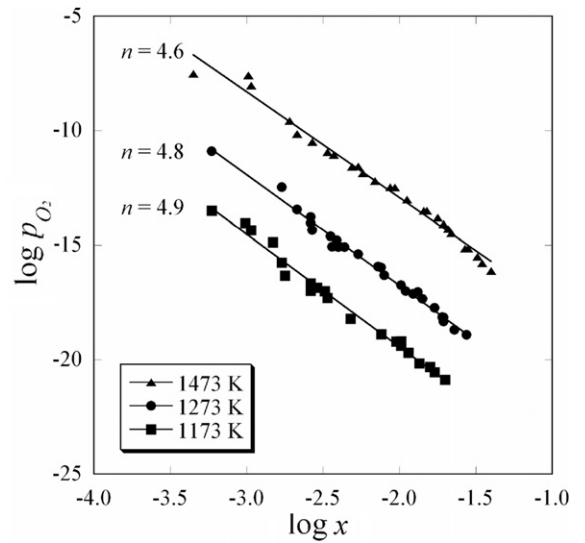


Fig. 3. Relationships between oxygen partial pressure and deviation from stoichiometry for  $(U_{0.80}Lu_{0.20})O_{2-x}$ .

Table 1

Slope of plots of oxygen partial pressure versus deviation from stoichiometry for  $(U,Gd)O_{2-x}$

Gd fraction	Temperature (K)	Slope $n$	Authors
0.14	1273	5	Une and Oguma [2]
0.14	1573	4	
0.27	1273	4	Lindemer and Sutton [5]
0.27	1573	3	
0.20	1273	5	Lindemer and Sutton [5]
0.30	1273	4	
0.30	1473	4	

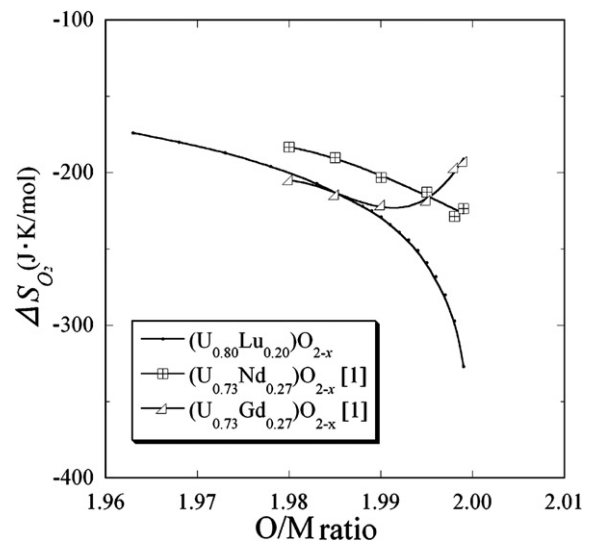


Fig. 4. Partial molar entropy of oxygen for  $(U_{0.80}Lu_{0.20})O_{2-x}$  as a function of O/M ratio.

$\Delta\bar{H}_{O_2}$  curves for  $(U,Gd)O_{2-x}$  and  $(U,Nd)O_{2-x}$  show steep increases, while that for  $(U_{0.80}Lu_{0.20})O_{2-x}$  shows a decrease. Although the reason for this behavior is unclear at present in spite of the similar defect structure deduced from the slope analysis, it might be caused by a different form in defect structures beyond the stoichiometry, namely in the hyper-stoichiometric range, between

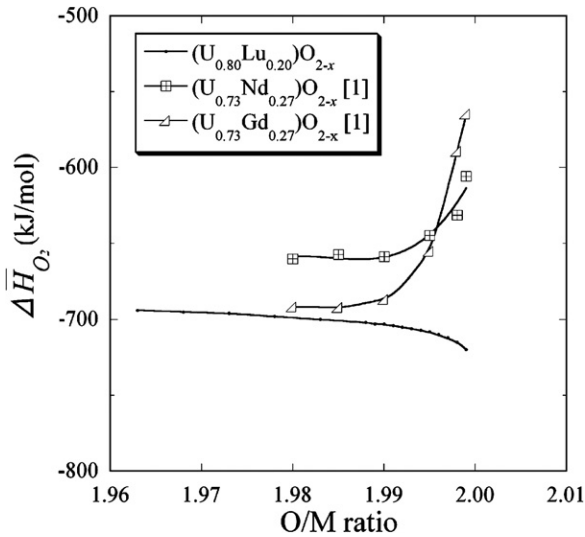


Fig. 5. Partial molar enthalpy of oxygen for  $(U_{0.80}Lu_{0.20})O_{2-x}$  as a function of O/M ratio.

$(U_{0.80}Lu_{0.20})O_{2-x}$  and  $(U,Nd)O_{2-x}$  or  $(U,Gd)O_{2-x}$ . Since no marked discontinuities in the profiles of  $\Delta\bar{G}_{O_2}$ ,  $\Delta\bar{S}_{O_2}$  and  $\Delta\bar{H}_{O_2}$  as a function of O/M ratio can be seen for  $(U_{0.80}Lu_{0.20})O_{2-x}$  in the present O/M ratio range, it is believed that the oxygen-deficient fluorite-type structure is maintained from  $x = 0$  to 0.04, 1173 to 1473 K without any ordering, such as intermediate phase formations as observed in Ce–O system [18].

The similarity of defect structure between  $(U_{0.80}Lu_{0.20})O_{2-x}$  and other forms of RDU, especially  $(U,Gd)O_{2-x}$ , is attributable to the well-known similarity among RE elements; i.e. showing only trivalency in the solid is unique for most of the RE elements except for Ce, Eu, Pr or Tb that show multi-valency. Therefore, the differences of absolute  $\Delta\bar{G}_{O_2}$  values between  $(U,Lu)O_{2-x}$  and  $(U,Nd)O_{2-x}$ ,  $(U,Gd)O_{2-x}$  or  $(U,Er)O_{2-x}$  could not be derived from different defect structures between them. Rather, it could be derived from stabilities of the oxygen vacancy in the  $UO_2$  fluorite lattice with oxygen hypo-stoichiometry. Namely, in the hypo-stoichiometric range, it can be said that the higher the  $\Delta\bar{G}_{O_2}$  value is at a constant O/M ratio, the higher the stability of the oxygen vacancy in the  $UO_2$  fluorite lattice should be. Such stability can be evaluated more precisely by a first-principle calculation for electronic structure of the RDU crystal. However, a calculation for a rather complex system like the present RDU, which consists of oxygen vacancies, RE-dopant and U ions are difficult at present mainly in terms of computer performance. One practical evaluation can be made by introducing the effective ionic radii [15]. In hypo-stoichiometric RE-doped ceria (RDC) systems, Yahiro et al. [19] found a relationship between reducibility of RDC and the effective ionic radii of various RE-dopants. In the case of RDU doped with Nd, Gd, Er and Lu, the effective ionic radius is the largest for Nd, second for Gd, third

for Er and smallest for Lu for oxygen coordination numbers of both 6 and 8 [15]. This order is the same as that for the  $\Delta\bar{G}_{O_2}$  of all forms of RDU considered here, although  $\Delta\bar{G}_{O_2}$  of  $(U,Nd)O_{2-x}$  are at the same level as those of  $(U,Gd)O_{2-x}$ . Therefore, there could be a certain relationship between the  $\Delta\bar{G}_{O_2}$  and the effective ionic radius for the RDU system. Although a quantitative discussion on such a relationship is difficult only from the present considerations, clues are given for construction of a practical prediction model for the  $\Delta\bar{G}_{O_2}$  of multi-elemental systems which consist of various RE-dopants, like the LDF.

#### 4. Conclusion

Oxygen potentials of  $(U_{0.80}Lu_{0.20})O_{2-x}$  were experimentally determined by thermogravimetric analysis using  $H_2O/H_2$  gas equilibria at 1173, 1273 and 1473 K. It was revealed that defect structure in  $(U_{0.80}Lu_{0.20})O_{2-x}$  was likely to be similar to that in other forms of rare earth-doped  $UO_2$ , although the oxygen potentials were higher. From this fact, together with considerations made using the effective ionic radii of rare earth dopants, it was concluded that the oxygen vacancy in hypo-stoichiometric Lu-doped  $UO_2$  had higher stability than that in the other forms of rare earth-doped  $UO_2$ .

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#### References

- [1] K. Une, M. Oguma, J. Nucl. Mater. 118 (1983) 189.
- [2] K. Une, M. Oguma, J. Nucl. Mater. 115 (1983) 84.
- [3] T. Matsui, K. Naito, J. Nucl. Mater. 138 (1986) 19.
- [4] H.S. Kim, Y.K. Yoon, M.S. Yang, J. Nucl. Mater. 209 (1994) 286.
- [5] T.B. Lindemer, A.L. Sutton Jr., J. Am. Ceram. Soc. 71 (1988) 553.
- [6] K. Une, M. Oguma, J. Nucl. Mater. 110 (1982) 215.
- [7] T.B. Lindemer, J. Brynstad, J. Am. Ceram. Soc. 69 (1986) 867.
- [8] T. Namekawa, K. Kawaguchi, K. Koike, S. Haraguchi, S. Ishi, in: Proceedings of the International Conference on GLOBAL2005, Tsukuba, Japan, October 9–13, 2005, paper No. 424.
- [9] S. Wang, H. Inaba, H. Tagawa, M. Dokiya, T. Hashimoto, Solid State Ionics 107 (1998) 73.
- [10] S. Wang, H. Inaba, H. Tagawa, T. Hashimoto, J. Electrochem. Soc. 144 (1997) 4076.
- [11] D. Schneider, M. Godickemeier, L.J. Gauckler, J. Electroceram. 1–2 (1997) 165.
- [12] T. Otake, H. Yugami, K. Yashiro, Y. Nigara, T. Kawada, J. Mizusaki, Solid State Ionics 161 (2003) 181.
- [13] T. Kobayashi, S. Wang, M. Dokiya, H. Tagawa, T. Hashimoto, Solid State Ionics 126 (1999) 349.
- [14] M. Osaka, K. Kurosaki, S. Yamanaka, J. Nucl. Mater. 357 (2006) 69.
- [15] R.D. Shannon, C.T. Prewitt, Acta Cryst. B25 (1968) 925.
- [16] C. Keller, H. Engerer, L. Leitner, U. Sriyotha, J. Inorg. Nucl. Chem. 31 (1969) 965.
- [17] O.T. Sorensen, Thermodynamics and defect structure of nonstoichiometric oxides, in: O.T. Sorensen (Ed.), Nonstoichiometric Oxides, Academic, New York, 1981, p. 1.
- [18] L. Manes, E. Parteli, C.M. Mari, Mater. Chem. 6 (1981) 417.
- [19] H. Yahiro, K. Eguchi, H. Arai, Solid State Ionics 36 (1989) 71.