The Lattice Parameter Behavior with Different Nd and O Concentration in the $(U_{1-y}Nd_y)O_{2\pm x}$ Solid Solution

Seung Min Lee [a], Travis W. Knight [a*], Stewart L. Voit [b], and Rozaliya I. Barabash [b]

[a] University of South Carolina, 300 Main Street, Columbia, SC 29208, United States

[b] Oak Ridge National Laboratory, United States

Abstract

The solid solution of $(U_{1-y}FP_y)O_{2\pm x}$ has the same fluorite structure as $UO_{2\pm x}$ and the lattice space is affected by dissolved fission products (FP) or oxygen concentration during irradiation. The relation between the lattice parameter and concentrations of neodymium and oxygen in the fluorite structure of $(U_{1-y}Nd_y)O_{2\pm x}$ was investigated by using X-ray diffraction (XRD). The lattice parameter behavior in the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution shows a linear change as a function of Oxygen to Metal ratio (O/M ratio) and solubility of neodymium. The lattice parameter depends on the radii of ions forming the fluorite structure and also can be expressed by a particular rule (modified Vegard's law). The numerical analyses of the lattice parameters for the stoichiometric and non-stoichiometric solid solution were conducted and the lattice parameter model for the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution was assessed. The major factors related to the lattice parameter change was also demonstrated in this work and showed good agreements when comparing the measured lattice parameter with the calculated lattice parameter.

[*] Corresponding author. Tel.: +1 803 777 1465.
Email: knighttw@cec.sc.edu

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I. Introduction

The irradiated UO_2 fuel contains various fission products and some of them such as zirconium, yttrium and lanthanides are soluble in the UO_2 structure [1]. This solid solution of the uranium dioxide-fission product oxide still forms the fluorite structure but the fission product oxide influences chemical and mechanical properties of the original UO_2 fuel. The unit cell of the UO_2 contracts or expands depending on the amount of the fission products and oxygen. In this work, $(U_{1-y}Nd_y)O_{2\pm x}$ samples were prepared for the study because Nd is the second highest yield of the major fission products (after zirconium) which form an oxide [1, 2]. The unit cell of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution is composed of cations, anions, and vacancies, while maintaining electrical neutrality. Neodymium in the UO_2 fluorite structure has a high solubility (about 80 mole percent in UO_2) [2, 3]. The experiments for the lattice parameter of the UO_2-rare earth oxide solid solution were performed previously [4, 5, 6]. In terms of the analyses of the previous experimental data, the lattice parameter decreases linearly as rare earth element concentration increases or oxygen concentration increases. So, the more detailed relation between lattice parameter and concentration of neodymium or oxygen for the hypo- and hyper-stoichiometry of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution was investigated after additional lattice parameter data were collected in this work. The lattice parameter as a function of neodymium concentration and O/M ratio was measured and compared to the literature. A very linear relationship between lattice parameter and Nd and O concentration for the stoichiometry and non-stoichiometry of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution was verified.

II. Experimental Procedure

II.A. Sample preparation

The powder type samples were prepared by Oak Ridge National Laboratory (ORNL). Table 1 shows four different neodymium concentration powder samples provided from ORNL. These samples are the U-Nd oxide compositions and were synthesized by the Modified Direct Denitration (MDD) process [7, 8]. Before the MDD process, the uranyl nitrate solution is prepared by dissolving a known weight of UO_2 in nitric acid and the neodymium nitrate solution is also prepared by dissolving a known weight of neodymium nitrate hexahydrate in water. These two solutions are mixed. Mixtures of the U-Nd parent batch are then prepared by weighing the solutions, and ammonium nitrate is added to the U-Nd weak nitric acid solution in a 2:1 of NH_4 to metal molar ratio. The mixed metal nitrate double salt passes through a perforated center tube and drips onto the wall of a heated rotating pipe. The solution dehydrates and begins to decompose as it travels down the heated pipe. The decomposition product is an amorphous solid oxide. The oxide is sieved and calcined in a furnace at 550^{o}C in an air purge gas to ensure complete conversion and to transform the product from an amorphous to crystalline solid. The decomposition process is oxygen rich so the oxide that is formed is a two-phase mixture and each phase is in the highest oxidation state (i.e. UO_3 and Nd_2O_3) [7, 8].

Each sample was pressed into a pellet in the glove box. A pellet was 13mm in diameter and 2mm in thickness. It was pressed at 280MPa for 5 minutes and weighed about 1.5g. After pressing, it was heated at 450°C for 5 hours to evaporate all moisture in the pellet and sintered in 4% H_2 – 96% Ar mixture gas at 1600°C for 5 hours in a

thermogravimetric analyzer (TGA) which can produce near stoichiometric $(U_{1-y},Nd_y)O_{2.0}$. When the product is heated at high temperature (>1200ºC) during reactive sintering, the two-phase mixture readily forms a single fluorite phase solid solution under reducing atmosphere (oxygen partial pressures) needed to achieve an oxygen stoichiometry of 2.0. Figure 1 shows the pellet sample both before sintering and after sintering.

II.B. Determination of the oxygen to metal ratio

To produce the stoichiometric and non-stoichiometric $(U_{1-y}Nd_y)O_{2.0\pm x}$ TGA (NETZSCH STA-409CD) was employed. First, a 2.0 point of the O/M ratio for each samples throughout the experiments must be found. To find the O/M ratio of 2.0, it is necessary to understand the typical oxygen partial pressure pattern for the oxide fuel. Figure 2 shows the typical sigmoidal curve of the oxygen partial pressure versus O/M ratio. In the typical pattern of the pO_2 versus O/M ratio for the single phase solid solution, stoichiometric $(U_{1-y}Nd_y)O_{2.0}$ has a range of the specific oxygen partial pressures for the O/M ratio of 2.0 as shown in Figure 2. Because of this range of the pO_2, it is possible to find a standard point of the stoichiometric $(U_{1-y}Nd_y)O_{2.0.}$ Here is an example for the procedure with TGA. An experiment starts with arbitrary pO_2 which is expected as a standard point. After the equilibrium state appears, it needs to use another pO_2 at the same temperature to reach another equilibrium state. If these two equilibrium states do not have any mass change, then they are in the range of the O/M ratio of 2.0 and can be used as standard points for other experiments to obtain non-stoichiometry. Next, an experiment starts with the stoichiometric $(U_{1-y}Nd_y)O_{2.0}$ and pO_2 is adjusted to obtain another equilibrium state which is driven to the non-stoichiometric $(U_{1-y}Nd_y)O_{2.0\pm x}$. After the non-stoichiometric $(U_{1-y}Nd_y)O_{2.0\pm x}$ is obtained, the sample is cooled down to room temperature

by 20-25˚C/min of the cooling rate at fixed low pO_2. It is expected that the sample is rarely oxidized during cooling at low oxygen partial pressure environment (lower than 10^{-6} atm) according to the Ohmichi et al. [4]. Finally, this sample can be used for the XRD experiment to determine the lattice parameter.

After different equilibrium states are measured, the O/M ratio can be calculated. The calculation of the O/M ratio for the $(U_{1-y}Nd_y)O_{2\pm x}$ Solid Solution is expressed in Equation 1 below.

$$\frac{O}{M} = \frac{\frac{actual\ weight\ of\ oxygen\ in\ a\ sample}{atomic\ weight\ of\ oxygen}}{\frac{actual\ weight\ of\ metal\ in\ a\ sample}{atomic\ weight\ of\ metal}} \qquad Eq.1$$

where M is U+Nd. Table 2 shows the experimental conditions in the TGA and O/M ratio results.

II.C. Lattice parameter measurement

After the O/M ratio is calculated, a XRD test (by Rigaku Ultima IV powder X-ray diffractometer) is performed to analyze the lattice parameter, to verify the calculated O/M ratio, and to confirm that the sample cooled down in the TGA is a single phase solid solution. The pellet sample used for the O/M ratio measurement was ground using the mortar and pestle. The particle size of the ground powder was less than 50 μm. XRD was operated at room temperature. The wavelength used was CuKα. The XRD pattern with intensity and diffraction angle (2θ) was obtained. Jade 5.0 software was used for the analysis of the XRD pattern and the lattice parameter. A lattice parameter can be correlated with and has been used to determine the O/M ratio. In general, a lattice parameter decreases as the O/M ratio increases or neodymium impurity increases [4, 5, 6]. Table 3 shows all

lattice parameter data used in this research and demonstrates the relationship between the O/M ratio and the lattice parameter in the $(U_{1-y}Nd_y)O_{2.0\pm x}$ solid solution.

III. Results and Discussion

III.A. Chemical composition and radii of ions in the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution

In this work, the lattice parameter behavior is distinguished by stoichiometry, and depends on Nd and O concentration. It is necessary to understand chemical compositions of ions in the solid solution. Ionic species are composed of U3+, U4+, U5+, U6+ and Nd3+ in the cation site and O2- and vacancy in the anion site. It is assumed that ionic species in the cation/anion site are mixed randomly but the unit cell maintains electrical neutrality. For better understanding, the fraction of ionic species was calculated. To calculate the fraction of ionic species thermochemical modeling (by three sub-lattice model) for the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution single phase was carried out using a thermochemical software and database package (FactSage) [10, 11]. After Gibbs free energy of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution single phase was optimized by the oxygen potential, phase equilibria, heat capacity and enthalpy increment, it was able to calculate the fraction of ionic species [10, 11]. Figure 3 shows the calculated ion fraction in the solid solution for the stoichiometry and Figure 4 shows the calculated ion fraction for the non-stoichiometry. In Figure 3 and 4 each line shows a different ionic species in the sub-lattice where y' is the second sub-lattice, y" is the third sub-lattice, and Va is vacancy. As shown in Figure 3, U3+ does not affect the unit cell much, and vacancy has an impact on the unit cell only at high Nd concentration. Therefore, the stoichiometric $(U_{1-y}Nd_y)O_{2.0}$ solid solution can be expressed as $(U^{4+}_{1-2y}U^{5+}_{y}Nd^{3+}_{y})O^{2-}_{2.0}$ using their electrical valences.

When U4+ ions are replaced by Nd3+ ions, either oxygen vacancies are created around U4+, or U4+ is oxidized to U5+ or U6+ ions. However, substitution of U5+ or U6+ for U4+ is more dominant than vacancy creation. When hypo-stoichiomeric $(U_{1-y}Nd_y)O_{2-x}$ is considered, oxygen vacancy has to be used to compensate extra cation charges and U4+ is more dominant than U3+, U5+, or U6+ to maintain electrical neutrality as shown in Figure 4. Then it can be expressed as $\left(U_{1-2y+2x}^{4+}U_{y-2x}^{5+}Nd_y^{3+}\right)O_{2-x}^{2-} + O_x^{Va}$, where $x \approx \frac{y}{2}$. On the other hand, when hyper-stoichiometric $(U_{1-y}Nd_y)O_{2+x}$ is considered, excess oxygen ions are occupied in the interstitial sites and vacancy area decreases. In addition, U5+ or U6+ is more dominant than U4+ or U3+ to compensate extra negative charges as shown in Figure 4. So, it can be expressed as $\left(U_{1-2y-2x}^{4+}U_{y+2x}^{5+}Nd_y^{3+}\right)O_{2+x}^{2-} - O_x^{Va}$.

Now, all three cases have a particular rule for the relation between the lattice parameter and Nd/O concentration in the solid solution according to Vegard's law. The unit cell of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution will be expanded or contracted by the change of cation and anion, and depends on the radii of ions [12]. Ohmichi et al. defined the lattice parameter of the $(U_{1-y}R_y)O_{2.0}$ solid solution in their research using the fraction of ion and radius of ions (where, R means rare earth elements) [4]. The comprehensive lattice parameter rule for the $(U_{1-y}R_y)O_{2.0}$ solid solution is expressed in Equation 2. Ninic et al. also assessed the lattice parameter of the Cerium Oxide based solid solution depending on Vegard's law [12].

$$a = \frac{4}{\sqrt{3}}\left(\sum_i X_{Ci}r_{Ci} + \sum_i X_{ai}r_{ai}\right) \qquad Eq.2$$

where, X is the fraction, r is the radius, ci means cation and ai means anion. The constant $\frac{4}{\sqrt{3}}$ in the equation is originated from the close-packed direction of the fluorite structure

which is the body diagonal of the unit cell. The body diagonal has $\sqrt{3}a$ and about ¼ of the body diagonal has half of the cation and half of the anion. So, the lattice parameter, a is equivalent to $\frac{4}{\sqrt{3}}(cation\ radius + anion\ radius)$. This specific rule can be applied to both stoichiometry and non-stoichiometry using the fraction of ions and radii of ions. In addition, ionic radii of uranium, neodymium, oxygen, and oxygen vacancy were analyzed by Ohmichi [4] and Shannon [13] as shown in Table 4.

When UO_2 contains Nd fission product of more than 50% in the solid solution, U6+ can be more involved in the unit cell and affect the lattice parameter more as demonstrated in Figure 3. Therefore, the radius of the U6+ ion has to be applied in Vegard's law for the very high Nd concentrated solid solution.

III.B. The lattice parameter behavior with Nd concentration in the stoichiometric ($U_{1-y}Nd_y)O_{2.0}$

The lattice parameter calculation using Vegard's law for the stoichiometric $(U_{1-y}Nd_y)O_{2.0}$ is derived from Equation 2 and is expressed in Equation 3.

$$a = \frac{4}{\sqrt{3}}\{(1-2y)r_{U4+} + yr_{U5+} + yr_{Nd3+} + r_{O2-}\}\times\left(1 - \frac{Nd\ concentration}{200}\right) \quad Eq.3$$

where y is the neodymium concentration and r is the radius of the ion. However, when the theoretical lattice parameter is applied for the $(U_{1-y}Nd_y)O_{2.0}$ solid solution, the correction factor, $(1 - \frac{Nd\ concentration}{200})$, needs to be added to the equation to reduce deviation and to correspond with the measured lattice parameter because of the impact of the soluble neodymium fission product in the UO_2 structure. The correction factor is based on the empirical analysis. Figure 5 is the plot of comparison between the calculated lattice parameter using Equation 3 and the measured lattice parameter from the XRD

experiments. The measured lattice parameter data from this work have good agreements with the calculated value. From the analysis of the lattice parameter versus Nd concentration, it is shown that the lattice parameter decreases linearly as Nd concentration increases in the (U1-yNdy)$O_{2.0}$ solid solution until maximum solubility. Two phases were observed after about 80% of Nd concentration in the solid solution [3, 14].

Figure 6 shows XRD patterns of the different Nd concentration samples for the stoichiometric ($U_{1-y}Nd_y$)$O_{2.0}$. Each XRD pattern was compared with the pure UO_2 XRD pattern, and it was observed that each XRD pattern has exactly the same pattern as the pure UO_2 XRD pattern but peak position slightly moves toward a higher 2 theta (2θ) as Nd concentration increases. When U4+ is replaced by Nd3+, which is larger than U4+, and Nd3+ expands the lattice space, other U4+ near Nd3+ is oxidized to U5+ due to electrical neutrality. However, U5+, which is smaller than U4+, contracts the lattice space more and eventually the lattice parameter in the unit cell decreases. For this reason, a higher angle of X-ray incidence is required to detect the smaller lattice distance. From Figure 6 it is also possible to know that there is no phase singularity from all the experimental data. In other words, there is no other phase or any impurity in the sample cooled down at low pO_2 environment in the TGA.

III.C. The lattice parameter behavior with O/M ratio in the non-stoichiometric ($U_{1-y}Nd_y$)$O_{2\pm x}$

After non-stoichiometric samples were prepared in the TGA, lattice parameters were measured likewise. The lattice parameter calculation using Vegard's law for the

non-stoichiometric $(U_{1-y}Nd_y)O_{2\pm x}$ is also derived from Equation 2. Equation 4 is for the hypo-stoichiometry and Equation 5 is for the hyper-stoichiometry.

$$a = \frac{4}{\sqrt{3}}\left\{(1-2y+2x)r_{U4+} + (y-2x)r_{U5+} + yr_{Nd3+} + \frac{(2-x)}{2}r_{O2-} + \frac{x}{2}r_{OV}\right\} \times \left(1 - \frac{Nd\ concentration}{200}\right) \quad Eq.4$$

$$a = \frac{4}{\sqrt{3}}\left\{(1-2y-2x)r_{U4+} + (y+2x)r_{U5+} + yr_{Nd3+} + \frac{(2+x)}{2}r_{O2-} - \frac{x}{2}r_{OV}\right\} \times \left(1 - \frac{Nd\ concentration}{200}\right) \quad Eq.5$$

where, y is the neodymium concentration and x is the oxygen concentration and r is the radius of the ion. In the Equation 4 and 5, the same correction factor based on the empirical analysis as Equation 3 is used to reduce a deviation and to correspond with the measured lattice parameters. Figure 7 and 8 are the plots of comparisons between the measured lattice parameter and the calculated lattice parameter using Equation 4 and 5 respectively. As a result, lattice parameter increases when O/M ratio decreases and also oxygen concentration in the UO_2 solid solution affects the lattice parameter. One thing to note here is that the theoretical lattice parameter using Vegard's law for the $(U_{1-y}Nd_y)O_{2.0\pm x}$ solid solution needs to apply the correction factor which is related to the concentration and atomic size of Nd. The correction factor for the lattice parameter will be different according to the soluble fission product elements in the UO_2 solid solution because of their different ionic sizes.

Figure 9 shows XRD patterns of the different O/M ratios. XRD peak slightly moves toward a higher 2θ as O/M ratio increases. This is showing the same phenomenon as that with different Nd concentration from the previous section. U4+ is oxidized to U5+ due to

electrical neutrality when more oxygen ions are introduced into the lattice space. Then this ionic change contracts the lattice space and eventually the lattice parameter decreases. For the same reason, a higher angle of X-ray incidence is needed to detect the smaller lattice distance. Figure 9 also proves that there is no other phase or any impurity in the sample.

IV. Conclusions

The soluble fission products, oxygen ions, or oxygen vacancies affect the crystal lattice of the UO_2 fluorite structure because uranium ions near fission products and oxygen ions change valence for electrical neutrality, and those ions have different ionic radii. In order to determine the lattice parameter behavior with different composition of neodymium and oxygen in the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution, XRD experiments were performed and results were analyzed. A nearly linear lattice parameter change was observed in the fluorite structure of the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution until the maximum solubility of neodymium. The relation between lattice parameter and neodymium concentration or O/M ratio is expressed by a particular rule related to Vegard's law for both the stoichiometry and the non-stoichiometry solid solution of $(U_{1-y}Nd_y)O_{2\pm x}$. However, experimental lattice parameter data did not match exactly Vegard's law and a certain additional term in Vegard's law was found by the empirical analysis. This additional term in Vegard's law which is the correction factor is related with concentrations and radii of ions. Therefore, applying the correction factor to Vegard's law for the $(U_{1-y}Nd_y)O_{2\pm x}$ solid solution is demanded and the correction factor depends on the soluble fission product elements in UO_2 because of their different atomic sizes. From the comparisons of the lattice parameters measured lattice parameters generally correspond with calculated lattice parameters applied by the correction factor. However,

some lattice parameter data from the literature has higher residual. It could be due to an error from measurement or inferior distribution of atoms in the structure during the sample preparation. More XRD data is required for the future work to verify literature data.

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