

Influence of Ce (III) Cation on Structural Property of Uranium Dioxide

Dong Woo Lee ^a, Jeongmook Lee ^a, Jong-Yun Kim ^{a,b} and Sang Ho Lim ^{a,b,*}

^aNuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 111, Daedeok-daero 989 Beon-gil, Yuseong-gu, Daejeon, 34057, Republic of Korea

^bDepartment of Radiochemistry & Nuclear Nonproliferation, University of Science and Technology, Gajeong-ro 217, Yuseong-gu, Daejeon, 34113, Republic of Korea

*Corresponding author: slim@kaeri.re.kr

1. Introduction

Studies of uranium oxides as nuclear fuels have been consistently investigate. For rare earth elements of fission products, there exists a solid solution state within the uranium oxide compounds [1].

There are various effects on the properties of UO_2 depending on the doped content and present in the matrix. Especially for Ce material, a fission product, it is used to study the structural form on uranium oxides because its structural properties are similar to plutonium material [2].

Commonly, Ce cation exists a multivalent type having both charges of oxidation state forms: 3^+ and 4^+ . In addition, the eight-coordination environment of Ce^{3+} cation, the ionic radius is similar to U^{4+} cation (Ce^{3+} ; 1.14Å, U^{4+} ; 1.0 Å) [3]. Therefore, it is difficult to identify structural changes when present in a solid solution state within UO_2 , but the lattice parameter is reduced due to oxygen vacancy [4-5].

The calculation of lattice parameter includes the whole powder pattern decomposition (Pawley and Le Bail) and the whole powder pattern fitting (Rietveld refinement) [6]. In the Rietveld method, the atomic coordinates are required for the calculations, refinement of profile and structural parameters [7].

In this study, cell parameter calculation methods are used to identify changes in the structural lattice according to the amount of Ce^{3+} doped in UO_2 .

2. Experimental

$\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ ($X = 0$ to 0.1) phases were synthesized through standard solid-state reactions. Stoichiometric amounts of UO_2 and CeO_2 were ground thoroughly with agate mortars and pestles and pressed into pellets. The pellets in alumina boats were gradually heated to 1700 °C for 18h in hydrogen atmosphere.

The X-ray powder diffraction data were collected on a Bruker D8-Advance diffractometer using $\text{Cu K}\alpha$ radiation at room temperature with 40 kV and 40 mA. The 2θ range was 20-120° with a step size of 0.02°, and a step time of 2s. The diffraction patterns were analyzed using Pawley, Le Bail and Rietveld method with the TOPAS program [8]. The Structural refinement of the materials was carried out in the space group $Fm-3m$ (no.225) with a starting model based on the reported data of UO_2 [9].

The lattice parameters were refined calculation methods, followed in subsequent iterations by the zero point error, unit-cell, peak shape, and temperature parameters. The energy-dispersive analysis by X-ray (EDAX) was carried out using JEOL JSM-6610LV.

EDAX for $\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ ($X = 0$ to 0.1) reveals U : Ce ratios of approximately 2 : 0, to 1.9 : 0.1, respectively.

3. Results and discussion

The structural determination of UO_2 has been extensively published. UO_2 crystallizes in the space group space group $Fm-3m$ (no.225). In the structural fluorite-type of UO_2 , U^{4+} cation is bonded to eight coordination environment. After synthesizing pure UO_2 , we were able to substitute the U^{4+} cation for Ce^{3+} up to $x = 0.1$ successfully to form $\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ ($X = 0$ to 0.1).

$\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ ($X = 0$, to 0.1) were not observed any crystallographic ordering between U^{4+} and Ce^{3+} cations. In the solid solutions of $\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ phases, the U^{4+} and Ce^{3+} were statistically disordered over the actinide metal sites. The powder XRD pattern for $\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ phases are shown in Fig. 1.

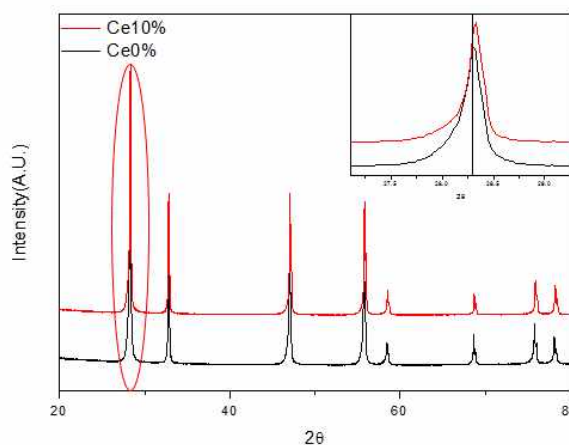


Fig. 1. Powder X-ray diffraction data for $\text{U}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ ($X = 0$, to 0.1).

See the Fig. 1. The diffraction peaks move to the right with increasing amounts of Ce^{3+} on the U^{4+} site, although, the larger ionic radius of Ce^{3+} compared with U^{4+} in eight coordination environment, which can be attributed to the oxygen vacancy [4-5].

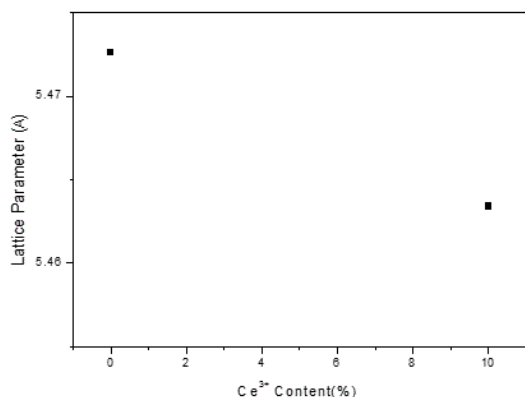


Fig. 2. Calculation by Rietveld refinement of lattice parameters as a function of the Ce occupancy for $U_{1-x}Ce_xO_{2-\delta}$ ($X = 0$ to 0.1).

To check the lattice parameters $U_{1-x}Ce_xO_{2-\delta}$ phases, whole powder pattern decomposition and fitting methods were used. As seen in Fig. 2, the calculation results show that experimental compounds cell parameter slightly decrease with increasing Ce^{3+} on the U^{4+} site.

4. Conclusions

The pure samples of $U_{1-x}Ce_xO_{2-\delta}$ phases have been synthesized using standard solid-solution techniques. The structures of the reported products were characterized by powder X-ray, EDAX, and fully analyzed using calculation methods (TOPAS). The substitution of Ce^{3+} cations into the UO_2 lattice is confirmed by lattice parameters from XRD patterns. It shows that presence of Ce-oxygen vacancies are decreasingly dominated in the work are applicable to interpret the oxidation behavior of spent nuclear fuel containing various fission products.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP; No.2012M2A8A5025925).

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