Chemical Properties of Hypo-Stoichiometric $U_{1-y}Nd_yO_{2-x}$ Produced by Neodymium Doping Into UO_2

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1. Introduction

Over the past decades, research on UO_2 fuel has been actively performed because it is nuclear fuel to be used in light water reactors (LWRs) [1-5]. The fission products generated from UO_2 under irradiation can affect the chemical properties of UO_2 [2-4]. In particular, the fission products such as Nd, Ce, La, and Pr were easily dissolved into UO_2 matrix at high temperature, to form solid solution, which influenced the fuel thermal conductivity and fuel performance [5]. Among these fission products, Nd was used as a representative trivalent element to study the effect of Nd on UO_2. In this study, the chemical properties of the hypostoichiometric Nd-doped UO_{2-x} pellets with various mol% Nd were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), and raman spectroscopy.

2. Experimental

Nd-doped UO_2 pellets with 0, 5.9, and 9.5 mol% Nd were prepared using UO_2 and Nd_2O_3 powders. The fabricated pellets with a diameter of 6.35 mm were sintered in an alumina tube furnace at 1700 °C for 18 h under H_2 atmosphere to produce hypostoichiometric $U_{1-y}Nd_yO_{2-x}$ pellets. SEM experiments were performed using a JEOL JSM-6610LV with an Oxford Instruments EDS. XRD data were obtained by Bruker-AXS D8 Advance system in the 2θ range of 20° to 120° with a scanning step of 0.02°/0.1s. Cu K_α radiation was used at beam current of 40 mA and beam generation power of 40 kV. The lattice parameter was calculated from the refinements of diffraction patterns based on a Pawley method using Bruker TOPAS program. ANDOR Shamrock SR500i Raman spectrometer with a He-Ne laser of 632.8 nm wavelength were used for Raman spectroscopic studies.

3. Results

Fig. 1 shows SEM images of Nd-doped UO_{2-x} pellets with 0, 5.9, and 9.5 mol% Nd. As shown in Fig. 1, the grain size of pellets decreased with higher Nd contents, which could be attributed to the lattice contraction of UO_2 by introducing Nd.

Raman spectrum of UO_{2-x} in Fig. 2a displayed two peaks at 445 and 1150 cm^{-1}, which corresponds to a cubic fluorite structure of uranium dioxide [6]. The band at 445 cm^{-1} was associated with the triple-degenerate Raman activity (T_{2g}) mode of U-O symmetric stretching mode in UO_2. In addition, the

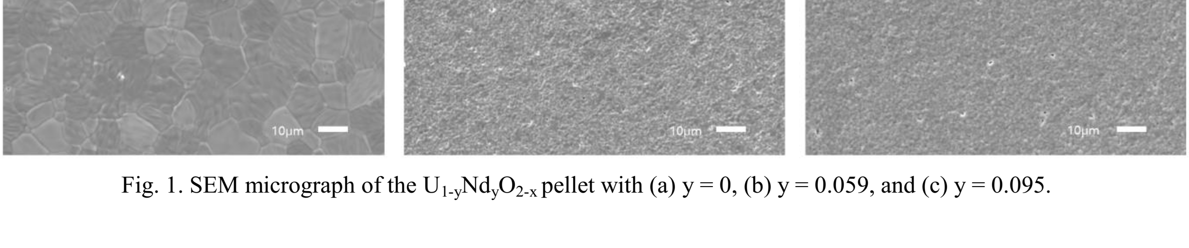

Fig. 1. SEM micrograph of the $U_{1-y}Nd_yO_{2-x}$ pellet with (a) y = 0, (b) y = 0.059, and (c) y = 0.095.

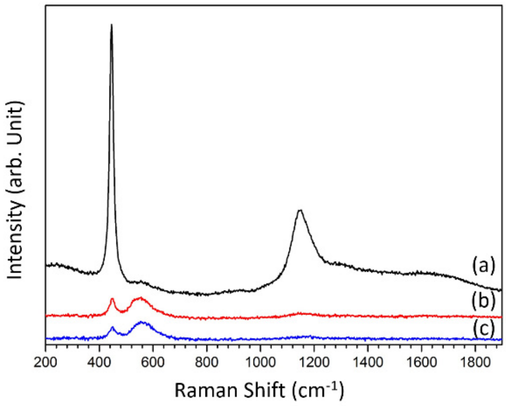

Fig. 2. Raman spectra of (a) UO_{2-x} and $U_{1-y}Nd_yO_{2-x}$ solid solutions with (b) y = 0.059 and (c) y = 0.095.

broad peak at 1150 cm^{-1} was assigned to the overtones (2L-O) of the primary L-O phonon (575 cm^{-1}). However, a new broad band appeared at 550 cm^{-1} as shown in Fig. 2b and 2c. As the concentration of Nd element in $U_{1-y}Nd_yO_{2-x}$ increased, the characteristic peaks of uranium dioxide at 445 and 1150 cm^{-1} decreased. On the other hand, the new signal at 550 cm^{-1} increased. These changes might be caused by the distortion of UO_2 crystal structure due to the introduction of Nd into the UO_2 matrix.

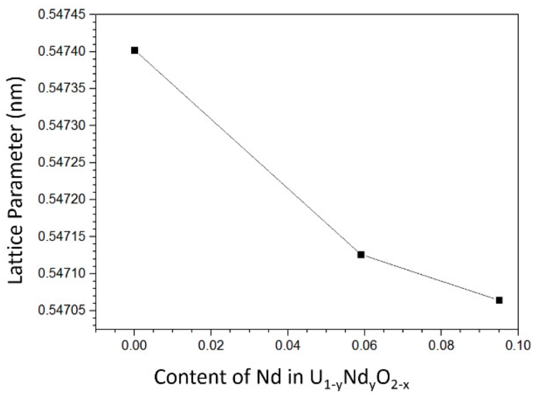

Fig. 3. Lattice parameters as a function of Nd content in $U_{1-y}Nd_yO_{2-x}$.

The lattice parameters of the $U_{1-y}Nd_yO_{2-x}$ were shown in Fig. 3. With the increase of Nd concentration in $U_{1-y}Nd_yO_{2-x}$ samples, their lattice parameters almost linearly decreased. In other words, when Nd was doped into UO_2, the U^{4+} around Nd^{3+} atoms can be oxidized to U^{5+}, leading to the reduction in the lattice parameter.

4. Conclusions

We have investigated the chemical properties of $U_{1-y}Nd_yO_{2-x}$ using SEM, Raman spectroscopy, and XRD. Their grain sizes decreased with increasing Nd doping rates. Raman spectroscopy results showed the distortion of UO_2 lattice structure due to Nd element. The lattice parameters obtained from the refinements of obtained diffraction patterns show the lattice contraction with increasing Nd doping rates, which were consistent with the results of Raman data.

ACKNOWLEDGEMENT

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (No. 2017M2A8A5014754)

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