Surface characterization of (U,Nd)O\textsubscript{2}: the influence of trivalent-dopant on structure of UO\textsubscript{2}  

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The surface structures of (U,Nd)O\textsubscript{2} pellets were characterized by using Raman spectroscopy to study the influence of trivalent-dopant on a UO\textsubscript{2} surface lattice. The stoichiometry of each sample pellet was confirmed by analyzing the lattice parameter calculated from X-ray diffraction spectra. Raman spectra of the sample pellets showed the defect structures related to oxygen vacancies. The concentration of oxygen vacancies in (U,Nd)O\textsubscript{2} pellets is affected by the Nd doping level.

Keywords: uranium dioxide; neodymium doping; X-ray diffraction; Raman spectroscopy; oxygen vacancy; surface structure

1. Introduction

In the spent nuclear fuel (SNF) of a PWR, several actinide (An) and lanthanide (Ln) elements were dissolved in a UO\textsubscript{2} matrix like (U,An)O\textsubscript{2} or (U,Ln)O\textsubscript{2} solid solutions [1-4]. Those elements have affected the physical and chemical characteristic of SNF such as the structural change of fuel surface and the chemical states of uranium. For example, the structural activation site on the surface of SNF can strongly induce its corrosion or chemical reaction with ground water under a failure of the barrier [2]. It is thus important to identify the surface characteristics of SNF to understand the related surface reaction of SNF. There have been many efforts to characterize the influence of several elements on the surface structure of UO\textsubscript{2} using simulated fuels systemically [5-10]. Those efforts are very helpful to understand the surface structural properties of SNF.

In this paper, (U,Nd)O\textsubscript{2} as a simple simulated fuel has been investigated using X-ray diffraction and Raman spectroscopy to study the influence of a trivalent-dopant on the surface structure of UO\textsubscript{2}. Nd is a major trivalent element formed in spent nuclear fuel [11,12]. The effect of Nd-doping on the UO\textsubscript{2} structure was analyzed and compared with previous published studies. This study aims to provide important implications for interpretation of defect structure caused by trivalent doping in uranium dioxide.

2. Experimental Section

UO\textsubscript{2} and Nd\textsubscript{2}O\textsubscript{3} powders were used as starting materials. The calculated amount of both powders for UO\textsubscript{2}, U\textsubscript{0.99}Nd\textsubscript{0.01}O\textsubscript{2-x} and U\textsubscript{0.95}Nd\textsubscript{0.05}O\textsubscript{2-x} were ground and mixed in an agate mortar. The powder mixtures were compacted to a round pellet with ~ 1 mm thickness. The pellets were sintered under a reducing condition with flowing hydrogen at 1700 °C for 18 h and followed by annealing under the same condition at 1200 °C for 12 h. The sintered pellets were placed in a vacuum container to prevent surface oxidation.

UO\textsubscript{2} and U\textsubscript{1-y}Nd\textsubscript{y}O\textsubscript{2-x} pellets were characterized by X-ray diffraction (XRD) using a Bruker AXS D8 Advance Xray Diffractometer with CuKa radiation. XRD data were collected within the range of 20 to 120°. The lattice parameters were calculated through the Pawley refinement process using the TOPAS software (Version 4.2) of Bruker.

Raman spectroscopy was also applied to measure the surface structure of the sample pellets with an ANDOR Shamrock SR500i spectrometer. The laser with a wavelength of 632.8 nm from a He-Ne laser was focused onto the sample through a 50-fold magnification lens in an Olympus microscope. Raman spectra were measured at five different positions on the surface over the range 400 ~ 1200 cm\textsuperscript{-1} with an exposure time of 100 s.

3. Results and discussion

The lattice parameters of all sample pellets refined from their XRD spectra are shown as black square dots in Figure 1. Those values linearly decrease as the Nd doping level increases. This linear relationship was well-matched with the case of U\textsubscript{1-y}Nd\textsubscript{y}O\textsubscript{2-y/2} type rather than that of U\textsubscript{1-y}Nd\textsubscript{y}O\textsubscript{2} type [13]. The analysis of
the lattice parameter indicated that the manufactured pellets in this study have hypo-stoichiometric form. The $U_{0.95}Nd_{0.05}O_{2-x}$ pellet, however, was somewhat deviated from the $U_{1-y}Nd_{y}O_{2-y/2}$ type to $U_{1-y}Nd_{y}O_{2}$ type. This deviation might be from a lack of reducing power during sintering for higher doping contents.

Raman spectra of the $UO_2$, $U_{0.99}Nd_{0.01}O_{2-x}$ and $U_{0.95}Nd_{0.05}O_{2-x}$ pellets are shown in Figure 2. These are the averaged spectra from five different positions on the surface of the pellets. The intensity of the peak at $\sim 445$ cm$^{-1}$ assigned as the U-O symmetric stretching (T$_{2g}$ mode) of the $UO_2$ fluorite structure [14-16] and that of the broad peak at $\sim 1150$ cm$^{-1}$ representing quasi-perfect fluorite structure of $UO_2$ [17,18] distinctly decrease with the increase in Nd content. On the other hand, the intensity of the broad band between 500 and 700 cm$^{-1}$ dramatically increases with increasing Nd concentration. These distinct features have been ascribed to the $UO_2$ lattice distortion due to the existence of defect structures or lattice damage [5-10,18].

To thoroughly interpret the lattice distortion of $U_{1-y}Nd_{y}O_{2-x}$ pellets, the Raman spectra in Figure 2 were analyzed in detail. Raman spectra for $U_{0.99}Nd_{0.01}O_{2-x}$ and $U_{0.95}Nd_{0.05}O_{2-x}$ pellets between 400 and 700 cm$^{-1}$ were deconvoluted into four Lorentzian peaks at $\sim 445$, $\sim 535$, $\sim 575$ and $\sim 630$ cm$^{-1}$ as shown in Figure 3. The peak at $\sim 535$ cm$^{-1}$ has been attributed to the oxygen vacancies [5-9]. This peak was also interpreted as a local phonon mode associated with an oxygen-vacancy-induced lattice distortion [5] and observed in the Raman spectra of Gd-, Dy-doped $UO_2$ [6], $U_{1-y}La_{y}O_{2-y/2}$ [7], and (U,Am)O$_{2-\delta}$ [8], $U_{1-y}Gd_{y}O_{2}$ [9] samples. The important point is that the peak related the oxygen vacancies is only observed in trivalent-doping $UO_2$ and not tetravalent-doping $UO_2$ like (U,Th)O$_2$ [10].

For trivalent-doping $UO_2$, the $3^+$ oxidation state of trivalent-dopant substituted for U($IV$) in $UO_2$ lattice can make oxygen vacancies to preserve electroneutrality in $U^{3+}_{1-x-y}M^{3+}_{x+y}O_{2+y/2-x/2}$. However,
there is less chance to create oxygen vacancies for \( U^{4+} \cdot \cdot \cdot M^{4+} \cdot \cdot \cdot O^{2-} \) in which U(IV) was simply replaced with stable M(IV). This interpretation could expect that the oxygen vacancy concentration increases as the doping level increases. Figure 4 shows that the area ratio between peaks at \(~535\) and \(~445\) cm\(^{-1}\), representing the relative concentration of oxygen vacancies in the UO\(_2\) fluorite lattice structure, increases with Nd doping level. A similar feature was also observed in the case of U\(_{1-y}\)La\(_y\)O\(_{2+y/2}\) [7], and U\(_{1-y}\)Gd\(_y\)O\(_{2-x}\) [9] samples. These results fully support that the influence of trivalent-dopant on the structure of UO\(_2\) is the creation of an oxygen vacancy and its concentration is systemically related to the trivalent-doping level. The peak at \(540\) cm\(^{-1}\) in the Raman spectrum of SIMFUEL [6], attributed to the oxygen vacancies, could be strongly induced from the influence of trivalent-dopants in the UO\(_2\) lattice.

The peak at \(~575\) cm\(^{-1}\) has been attributed to a first-order longitudinal optical (L-O) phonon mode [17,18]. Although this mode is originally forbidden in the perfect fluorite structure of UO\(_2\), it is allowed under the break down of selection rule from low symmetry due to a crystal lattice disorder [17]. The oxygen vacancies in U\(_{1-y}\)Nd\(_y\)O\(_{2-x}\) pellets could induce a lattice disorder, and thus first-order L-O Raman modes are allowed, as shown in Figure 3.

The peak ascribed to the presence of U\(_3\)O\(_5\) due to surface oxidation was rarely observed at \(~630\) cm\(^{-1}\) [19]. This confirms a marginal surface oxidation of U\(_{0.99}\)Nd\(_{0.01}\)O\(_{2-x}\) and U\(_{0.95}\)Nd\(_{0.05}\)O\(_{2-x}\) pellets.

### 4. Conclusion

To characterize the influence of trivalent-dopant on the surface structure of UO\(_2\), the surface of U\(_{1-y}\)Nd\(_y\)O\(_{2-x}\) pellets was analyzed using XRD and Raman spectroscopy techniques. The lattice parameters calculated from XRD spectra confirm the hypo-stoichiometric form of U\(_{1-y}\)Nd\(_y\)O\(_{2-x}\). Raman spectra of U\(_{0.98}\)Nd\(_{0.02}\)O\(_{2-x}\) and U\(_{0.95}\)Nd\(_{0.05}\)O\(_{2-x}\) pellets show the creation of the oxygen vacancies on the surface lattice and the increasing oxygen vacancy concentration with increasing Nd doping level. These results combined with published literature confirm that trivalent-dopants including Nd strongly affect the surface structure of UO\(_2\) with oxygen vacancies created owing to a charge compensation. The characterization of (U,Nd)O\(_{2-x}\) surface structures can provide important implications for characterizing the surface of SNF.

### Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2017M2A8A5014754).

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