

## Surface Characterization of Metal Doped Uranium Dioxide: Comparison of Trivalent- and Tetravalent-doping effect

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### 1. Introduction

Microstructure and components of spent nuclear fuel (SNF) are totally different from initial  $\text{UO}_2$  fuel before irradiation. Because of formation of fission products, transuranium elements and activation products, physical and chemical properties of  $\text{UO}_2$  matrix were changed [1-3]. Especially, Non-stoichiometry and rare earth/actinides/lanthanides doping on SNF could cause the distortion of  $\text{UO}_2$  cubic matrix and change of the chemical reactivity [4,5]. These effects would provide the surface activation site that could enhance chemical reactions and corrosion processes. Therefore, it is important to characterize the surface structures and properties of SNF when the final strategy for the disposal of SNF is considered with the failure case of barrier [3].

In this study, the surface structures of various simulated fuels instead of SNF were characterized using X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Nd (or Gd) is one of the major fission products and selected as representative trivalent dopants. Th is selected as a model element of tetravalent dopant. The influences of trivalent- and tetravalent-doping on the surface structure of  $\text{UO}_2$  matrix are compared and discussed.

### 2. Experimental sections

Calculated amounts of  $\text{UO}_2$  and  $\text{Nd}_2\text{O}_3$  (or  $\text{Gd}_2\text{O}_3$ ,  $\text{ThO}_2$ ) powders for  $\text{U}_{1-y}\text{Gd}_y\text{O}_2$  (or  $\text{U}_{1-y}\text{Gd}_y\text{O}_2$ ,  $\text{U}_{1-y}\text{Th}_y\text{O}_2$ ) were weighed and blended. The powder mixtures were pelletized by compressing. The sample pellets were sintered in the tube furnace at 1700 °C for 18 h with hydrogen atmosphere. The sintered pellets were cooled to room temperature after annealing while maintaining hydrogen atmosphere at 1200 °C for 12 h. In this condition, it is expected that  $\text{U}^{4+}_{1-y}\text{Nd}^{3+}_y\text{O}_{2-y/2}$  type should be manufactured for Nd (or Gd) doped  $\text{UO}_2$ .  $\text{UO}_2$  pellet was manufactured under similar procedure.

X-ray diffraction (XRD) method was applied to obtain the lattice parameter of sample pellets. Bruker D8 Advance using  $\text{CuK}\alpha$  line source filtered with a Ni foil (beam current 40mA at 40kV) was used to take XRD spectra. The lattice parameters of the samples

were calculated from XRD spectra with refinement process.

The surface morphologies of sample pellets were measured by scanning electron microscopy (SEM). SEM images were obtained using electron acceleration of 20 keV.

Raman spectroscopy was used to characterize the surface structure of each pellet. Raman spectra were obtained using ANDOR Shamrock SR500i spectrometer with a wavelength of 632.8 nm from He-Ne laser and analyzed by peak deconvolution method.

### 3. Results

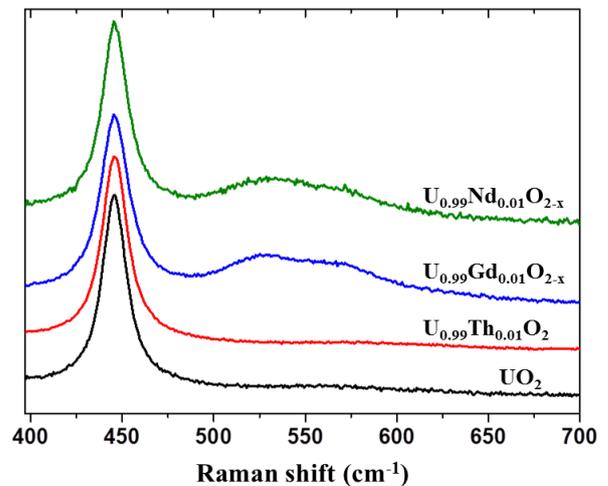


Fig. 1. Raman spectra of  $\text{UO}_2$  (black line),  $\text{U}_{0.95}\text{Th}_{0.01}\text{O}_2$  (red line),  $\text{U}_{0.95}\text{Gd}_{0.05}\text{O}_{2-x}$  (blue line) and  $\text{U}_{0.95}\text{Nd}_{0.05}\text{O}_{2-x}$  (green line) pellets from bottom to up.

The lattice parameters for  $(\text{U,Th})\text{O}_2$ ,  $(\text{U,Gd})\text{O}_2$  and  $(\text{U,Nd})\text{O}_2$  were linearly changed with increasing doping level and followed Vegard's law [6]. These linear relationships indicate that sample pellets were made as solid solutions with remaining  $\text{UO}_2$  fluorite structure. For  $(\text{U,Gd})\text{O}_2$  and  $(\text{U,Nd})\text{O}_2$ , it was confirmed that they existed as hypo-stoichiometric form.

The grain size for  $(\text{U,Gd})\text{O}_2$  and  $(\text{U,Nd})\text{O}_2$  in SEM images decreased with increasing dopant content and had similar features each other. For  $(\text{U,Th})\text{O}_2$ , there was no significant change of the grain size with Th doping level. These features could be caused by size of doping

element. While the size of Nd and Gd elements are smaller than U, that of Th is slightly larger than U.

Raman spectra of  $U_{0.99}Th_{0.01}O_2$  and  $UO_2$  have no difference as shown in Fig. 1. However, there are defect structures related to oxygen deficiency in Raman spectra of  $U_{0.99}Gd_{0.01}O_{2-x}$  and  $U_{0.99}Nd_{0.01}O_{2-x}$  at the range of 500 to 650  $cm^{-1}$ . For (U,Th) $O_2$ ,  $Th^{4+}$  just replaced  $U^{4+}$  in  $UO_2$  with no charge change, therefore it is hard to generate the oxygen deficiency [7]. For (U,Gd) $O_2$  and (U,Nd) $O_2$ , on the other hand,  $Gd^{3+}$  (or  $Nd^{3+}$ ) replacing  $U^{4+}$  under reducing condition could make the oxygen vacancy in  $U^{4+}_{1-y}Gd^{3+}_yO^{2-}_{2-y/2}$  (or  $U^{4+}_{1-y}Nd^{3+}_yO^{2-}_{2-y/2}$ ) without oxidation of  $U^{4+}$  to  $U^{5+}/U^{6+}$  [8]. This oxygen vacancy should result in the lattice distortion of  $UO_2$  fluorite structure.

Summarizing these results, trivalent-dopant,  $Gd^{3+}$  or  $Nd^{3+}$ , induces the oxygen vacancy and the smaller grain size in  $UO_2$  surface structure and tetravalent dopant,  $Th^{4+}$ , has small influence on  $UO_2$  surface structure.

#### 4. Conclusions

To investigate the influence of trivalent- and tetravalent-doping on the surface structure of  $UO_2$ , (U,Th) $O_2$ , (U,Gd) $O_2$  and (U,Nd) $O_2$  were manufactured and analyzed using XRD, SEM and Raman spectroscopy. Experimental results showed that trivalent-doping induced more change of  $UO_2$  fluorite structure than tetravalent-doping. This behavior would be strongly related to chemical reactivity.

#### ACKNOWLEDGEMENT

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

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