

Study on Surface Structure of $U_{1-y}Gd_yO_{2-x}$ Using Raman Spectroscopy

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1. Introduction

During irradiation of UO_2 nuclear fuel in the reactor, fission products (FPs) including actinides, lanthanides, trans-uranium elements and activation products are produced and located in the fuel [1-3]. Those fission products are doped in the nuclear fuel as $(U,FP)O_{2\pm x}$ form. It is considered that $(U,FP)O_{2-x}$ or stoichiometric form is produced under reducing condition in very high burn-up [4]. To understand the structural character of the spent nuclear fuel, rare earth element (REE) doped $UO_{2\pm x}$ have been studied as simulated spent fuel. The REE doping effect has influence on the phase stability in U-FP-O system, thermal conductivity and the relevant fuel performance [5-8]. Raman spectroscopy has been used to investigate surface structure of the nuclear fuel materials, because of its sensitivity, convenience and non-destructive sample preparation [9]. The Raman studies on trivalent-doped UO_2 directly show the defect due to oxygen vacancy that could be created by loss of oxygen for charge compensation [10-12]. This defect has significant effect on the kinetics of fuel oxidation.

In this study, we have been investigated the effect on Gd-doping on the UO_2 structure with Raman spectroscopy to characterize the defect structure of nuclear fuel material.

2. Experimental Section

$U_{1-y}Gd_yO_{2-x}$ solid solution pellets with various compositions were prepared by a powder mixing solid-state reaction. Calculated amounts of Gd_2O_3 and UO_2 powder were thoroughly weighed and mixed using an agate mortar. Then, the mixture of powder was pressed into a pellet form and sintered at $1700^\circ C$ for 18 h in hydrogen atmosphere. After annealing in same atmosphere at $1200^\circ C$ for 12 h, the sintered pellets were cooled to room temperature in hydrogen flow condition. The UO_2 pellet was also prepared by same method.

X-ray diffraction (XRD) data of $U_{1-y}Gd_yO_{2-x}$ solid solution pellets were obtained in the range 20° to 120° (scan step 0.02°) by Bruker D8 Advance at room temperature. The $CuK\alpha$ line source filtered with a Ni foil (beam current 40mA at 40kV) was used. The lattice parameters of the samples were calculated from refinement process using TOPAS program.

Raman spectra were acquired using ANDOR Shamrock SR303i spectrometer with a 632.8nm excitation wavelength He-Ne laser. The spectrum was

acquired using an exposure 300 s over the wavenumber range from 398 to 1198 cm^{-1} . The laser was focused onto sample using an Olympus microscope with 50-fold magnification lens

3. Results

The lattice parameter of pellets refined from their XRD spectra linearly decreased as the Gd doping level increased, while Gd_2O_3 -dispersed UO_2 in which Gd_2O_3 particles are just dispersed in the UO_2 matrix showed no change in lattice parameter with increasing Gd content. Moreover, XRD patterns of $U_{1-y}Gd_yO_{2-x}$ pellets show fluorite-type structure without the peaks of monoclinic Gd_2O_3 . Those analyses of XRD data indicate that sintered pellets are formed as solid solutions. The linear relationship of the lattice parameter for these pellets is well-matched with that of $U_{1-y}Gd_yO_{2-x}$ ($x \approx y/2$)-type solid solutions [13]. The approximated oxygen-to-metal (O/M) ratio and oxygen deficiencies of $U_{1-y}Gd_yO_{2-x}$ pellets were calculated from the relation between the lattice parameter variations with x in $U_{1-y}Gd_yO_{2-x}$ type solid solution at constant Gd content [13]. The oxygen deficiency of pellet increased with increasing Gd contents.

Raman spectra of UO_2 and $U_{0.8}Gd_{0.2}O_{2-x}$ are shown in Fig. 1. Raman spectrum of pure UO_2 shows significant two peaks at $\sim 445\text{ cm}^{-1}$ and at $\sim 1150\text{ cm}^{-1}$ that were assigned to U-O symmetric stretching mode in the fluorite structure [14-16] and an overtone of the first order longitudinal optical (L-O) phonon mode regarded as fingerprint for quasi-perfect fluorite structure [17,18], respectively.

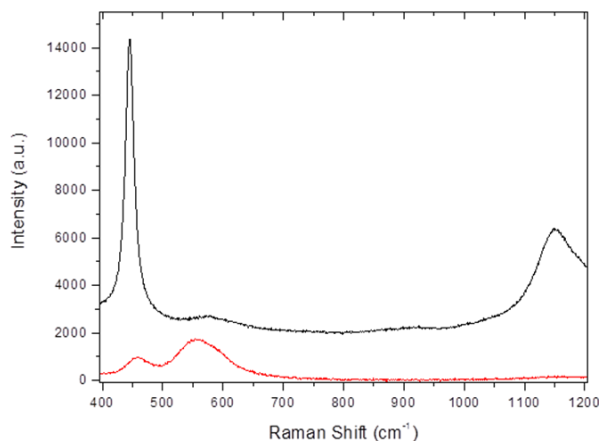


Fig. 1. Raman spectra of UO_2 (up, black line) and $U_{0.8}Gd_{0.2}O_{2-x}$ (bottom, red line) pellets at room temperature, respectively

Raman spectrum of $U_{0.8}Gd_{0.2}O_{2-x}$ shows significant difference with that of UO_2 . The intensities of two peaks at ~ 445 and ~ 1150 cm^{-1} markedly decrease, but the broad band in the region 500 to 650 cm^{-1} increase. The decreasing intensity of peaks at ~ 445 and ~ 1150 cm^{-1} means the lattice distortion of perfect fluorite structure. The broad band was deconvoluted to three peaks at ~ 530 , ~ 575 and ~ 630 cm^{-1} . The peaks at ~ 530 , ~ 575 and ~ 630 cm^{-1} were ascribed as defect due to oxygen vacancy associated with Gd^{3+} , first order L-O phonon mode due to crystal lattice disorder and formation of M_4O_9 during oxidation, respectively [10-12]. The relative ratio between the area of peaks at ~ 445 and ~ 530 cm^{-1} represents the approximated relative ratio of oxygen vacancies and fluorite lattice structure of UO_2 . This relative ratio increases with Gd concentration in $U_{1-y}Gd_yO_{2-x}$ solid solutions and calculated oxygen deficiencies.

4. Conclusions

The $U_{1-y}Gd_yO_{2-x}$ solid solution pellets with various Gd contents were prepared and investigated by XRD and Raman spectroscopy to investigate the defect structure and oxygen vacancies. The oxygen deficiencies of pellets were estimated by the relation between the doping concentration and a lattice parameter evaluated from XRD spectra. The Raman spectra of $U_{1-y}Gd_yO_{2-x}$ solid solution pellets show the distorted fluorite structure with defect structure due to oxygen vacancies with increasing Gd contents.

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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