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Raman study on structure of $U_{1-y}Gd_yO_{2-x}$ (y=0.005, 0.01, 0.03, 0.05 and 0.1) solid solutions

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HIGHLIGHTS

- Investigation of structural character of $U_{1-y}Gd_yO_{2-x}$ solid solutions.
- Defect structures in $U_{1-y}Gd_yO_{2-x}$ solid solutions were evaluated by Raman spectroscopy.
- Oxygen deficiency due to Gd content causes Raman band related to oxygen vacancy.

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ABSTRACT

The $U_{1-y}Gd_yO_{2-x}$ solid solutions with y = 0.005, 0.01, 0.03, 0.05 and 0.1 were characterized by Raman spectroscopy to investigate the defect structure induced by oxygen vacancies. The oxygen deficiencies of solid solutions were estimated by the relation between the doping level and a lattice parameter calculated from X-ray diffraction patterns. Raman mode shifts to higher wavenumber with increasing doping level showed that crystal lattice disorder due to oxygen vacancies. The frequency shifts and relative ratio of Raman modes were enabled to be the indicator for composition, defect and oxygen vacancy of $U_{1-y}Gd_yO_{2-x}$ solid solutions.

1. Introduction

In reactor irradiation of UO_2 nuclear fuel leads to the formation of a wide range of fission products, transuranium elements and activation products [1–3]. Among them rare earth (RE) elements form $U_{1-y}RE_yO_2$ solid solutions with UO_2 [4]. When irradiated under reducing circumstances, to a high burnup in the range of 70–80 GWd/tU, the UO_2 fuel becomes doped with fission products (FPs), especially rare earths, and can be considered as a slightly sub-stoichiometric ($U_{1-y}FP_yO_{2-x}$) or stoichiometric compound [5]. A knowledge of the structural character of RE-doped $UO_{2\pm x}$ is very important not only to understand the characteristics of spent nuclear fuel but also to describe the thermodynamic properties and the phase relations in U-RE-O systems [6–9]. Among the many RE elements, Gd is one of the major fission products formed in solid solution with UO_2 and has often been selected as a dopant in simulated spent nuclear fuels [10–12]. It is also used as a burnable absorber for the UO_2-Gd_2O_3 fuels developed to extend the length of the fuel cycle for PWRs [13]. Thus, Gd-doped UO_2 has been extensively researched using several experimental techniques, generally in tandem with X-ray diffraction (XRD) [14–20], to understand its physical and chemical properties.

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Recently, Raman spectroscopy has been widely applied to characterize nuclear fuel materials, because it is a convenient, sensitive and nondestructive method [21]. For example, the effect of oxygen stoichiometry on the defect structure of UO_2 [22,23], the oxygen sublattice structure in thorium dioxide-uranium dioxide fuel materials [24] and the influence of trivalent-dopants on the structural properties of UO_2 [25] have been investigated in detail using Raman spectroscopy. The role of oxygen vacancies on the kinetics of oxidation of fuel have also been demonstrated in Raman studies of Gd-, Dy-doped UO_2 [25], $U_{1-y}Nd_yO_{2-x}$ [26], $U_{1-y}La_yO_{2-y/2}$ [27], and $U_{1-y}Am_yO_{2-x}$ [28] samples. The oxygen vacancy can be created to maintain electroneutrality in RE(III)-doped UO_2 when RE(III) is substituted for U(IV) in solid solutions.

In this study we have characterized the effect of Gd-doping on the structure ($U_{1-y}Gd_yO_{2-x}$) using XRD and Raman spectroscopy to identify the possible defect structures in nuclear fuel materials. Defect structures of $U_{1-y}Gd_yO_{2-x}$ solid solutions with various Gd doping levels were analyzed, and the results compared with published literature.

2. Experimental

$U_{1-y}Gd_yO_{2-x}$ solid solution pellets with various composition (y = 0.005, 0.01, 0.03, 0.05 and 0.1) were synthesized by a conventional solid-state reaction with powder mixing. Appropriate amounts of UO_2 and Gd_2O_3 (Aldrich, >99.99%) powders to achieve the intended composition were blended thoroughly in an agar mortar. The mixtures were then pressed into a disk-shaped pellet and sintered in an alumina tube furnace (Ajeon Heating Industrial, Korea) at 1700 °C for 18 h under a reducing atmosphere with flowing H_2 to produce $U^{4+}{}_{1-y}Gd^{3+}{}_yO^{2-}{}_{2-y/2}$ type solid solutions [8,15]. The sintered pellets were cooled to room temperature in flowing H_2 after annealing in the same atmosphere at 1200 °C for 12 h. An undoped UO_2 pellet was also prepared using the same procedure. After sintering, the pellets were stored in a vacuum chamber to prevent surface oxidation before measuring XRD and Raman spectra.

The X-ray diffraction (XRD) patterns of the $U_{1-y}Gd_yO_{2-x}$ solid solution pellets were performed using a Bruker AXS D8 Advance X-ray Diffractometer using CuKα radiation at room temperature. XRD data was collected in the range from 20° to 120° using a 0.02° step size. These analyses required the exposure of the specimens to air for a total time of only 500 s. Data was collected from several locations to confirm the solid structure was homogeneous. The lattice parameters were calculated by a refinement process using the TOPAS program (Bruker Analytical X-Ray Systems) with the $Fm\bar{3}\,m$ space group.

The Raman spectra were measured with an ANDOR Shamrock SR500i spectrometer, with active vibrations excited using a He-Ne laser with a wavelength of 632.8 nm. The laser with *c.a.* 5 mW power was focused onto the pellets using an Olympus microscope with a 50-fold magnification lens. This laser power was confirmed as low enough to prevent surface oxidation of the pellets due to local heating by the laser beam [29]. Raman spectra were acquired over the wavenumber range 400–1200 cm^{-1} at room temperature with an exposure time to air of 300 s. Raman spectra were measured at different locations on the surface of a pellet to confirm the homogeneity of the pellet and the reproducibility of the spectra.

3. Results and discussion

XRD patterns for UO_2 and a number of $U_{1-y}Gd_yO_{2-x}$ pellets with different Gd contents are shown in Fig. 1(a). All the specimens exhibit the fluorite structure and no XRD peaks for monoclinic

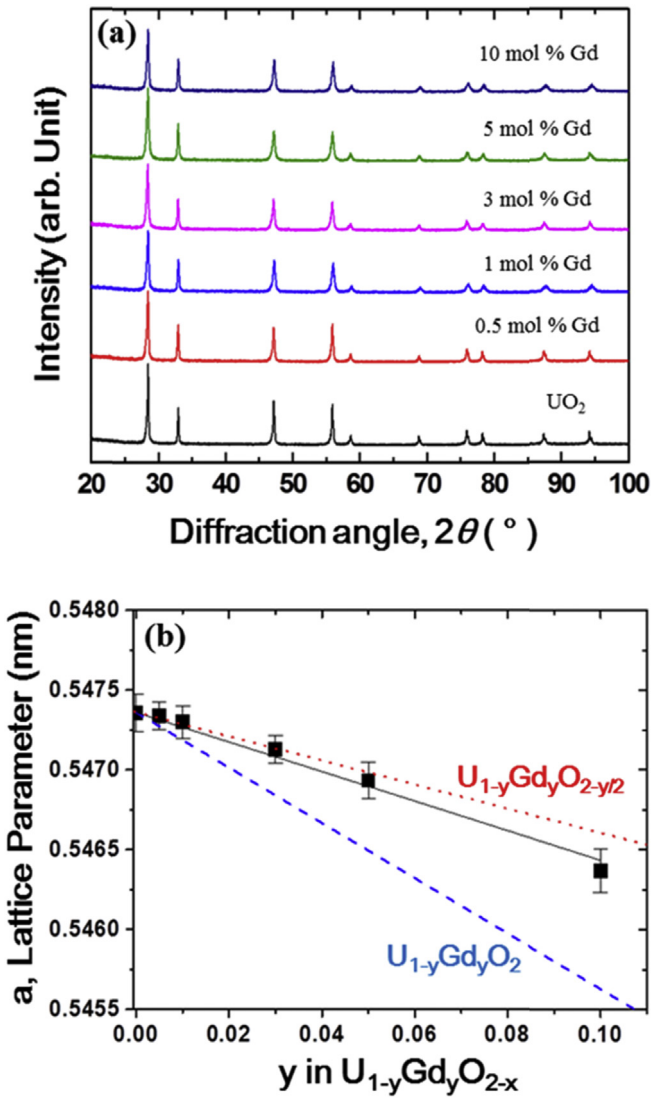

Fig. 1. (a) XRD patterns of UO_2 and $U_{1-y}Gd_yO_{2-x}$ solid solutions with y = 0.005, 0.01, 0.03, 0.05 and 0.1. (b) The lattice parameters obtained from XRD patterns of UO_2 and $U_{1-y}Gd_yO_{2-x}$ solid solutions with increasing Gd concentration. The red dotted and blue dashed lines show the linear relationships obtained for $U_{1-y}Gd_yO_{2-y/2}$ and $U_{1-y}Gd_yO_2$ solid solutions, respectively, as the Gd content changes [15]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Gd_2O_3 and undoped UO_2 were observed in the range $25° < 2\theta < 35°$ in contrast to patterns recorded on Gd_2O_3-dispersed UO_2 in which Gd_2O_3 particles are dispersed within the UO_2 matrix [30]. The lattice parameters of the pellets obtained from these patterns are plotted as a function of Gd content in Fig. 1(b). In contrast to the minor change in lattice parameter observed with increasing Gd content for the Gd_2O_3-dispersed UO_2 [30], the lattice parameter for the series $U_{1-y}Gd_yO_{2-x}$ solid solutions decreases linearly with the increase in Gd content. Our linear relationship for $U_{1-y}Gd_yO_{2-x}$ solid solutions is less steep than that observed for $U_{1-y}Gd_yO_2$-type solid solutions, but well-matched with that of $U_{1-y}Gd_yO_{2-x}(x \approx y/2)$-type solid solutions [15]. Lanthanide-doped UO_2 ($U_{1-y}La_yO_{2-y/2}$) solid solutions also exhibited a linear relationship between the lattice parameter and the lanthanum content [27]. This analysis shows our pellets are sub-stoichiometric $U_{1-y}Gd_yO_{2-x}(x \approx y/2)$ solid solutions in the given range y = 0.005–0.05.

Although it is quite difficult to measure the accurate oxygen-to-metal (O/M) ratio for rare earth-doped uranium dioxides, Ohmichi