Raman Study of Lattice-Doped Uranium Dioxide

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1. Introduction

UO_2 is a typical fuel material for the pressurized water reactor supplying sustainable nuclear energy. It is also known that many fission products and actinides are produced and located in the UO_2 after irradiation in the reactor [1-3]. To understand the structural character of the spent nuclear fuel, good knowledge of nuclear fuel material is required. Lattice-doped UO_2 samples have been used as simulated spent fuel and studied

Raman spectroscopy has been used to investigate surface structure of the nuclear fuel materials, because of its sensitivity, convenience and non-destructive sample preparation [4]. 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 [5-6].

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

2. Experimental

Lattice-doped UO_2 sample pallets were prepared by the sintering of a mixture of UO_2 and Gd_2O_3 (or Nd_2O_3, ThO_2, ZrO_2) powders with various compositions. The powder mixtures were pelletized and sintered at 1700℃ for 18 h in hydrogen atmosphere. The surface structure of the sample pellets was characterized using X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM).

XRD data was collected by Bruker D8 Advance using CuKα line source (beam current 40mA at 40kV). The lattice parameters of the samples were calculated from XRD spectra with refinement process. The morphologies of sample surface were also obtained by SEM.

Raman spectra were acquired using ANDOR Shamrock SR500i spectrometer with a 633 nm 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.

For Zr-doped UO_2, first-principles density functional theory (DFT) calculation was applied to interpret the Raman spectra.

3. Results

The lattice parameters of $(U,Gd)O_2$, $(U,Nd)O_2$, $(U,Th)O_2$, and $(U,Zr)O_2$ linearly increased or decreased as the doping level increased. These linear relationships represented that sample pellets were formed as a solid solution. The grain size observed in SEM images of $(U,Gd)O_2$, $(U,Nd)O_2$, and $(U,Zr)O_2$ decreased with increasing doping level. However, there was less change of the grain size with various Th doing levels in $(U,Th)O_2$. It is expected that the size of substituted cation was strongly related to that change of the grain size.
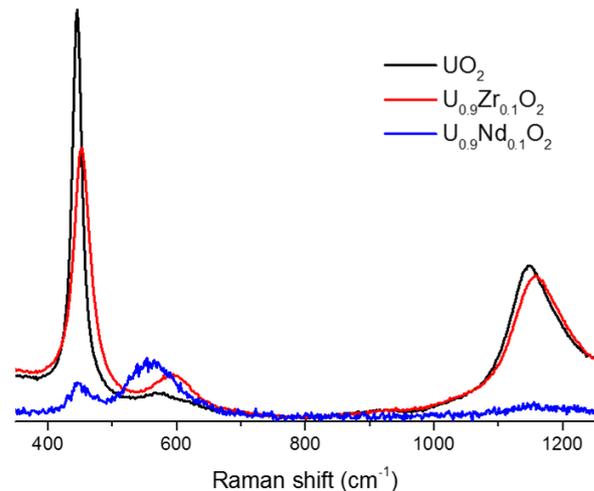
Fig. 1. Raman spectra of UO_2 (black line), $U_{0.9}Zr_{0.1}O_2$ (red line) and $U_{0.9}Nd_{0.1}O_2$ (blue line) pellets at room temperature, respectively

Raman spectra of UO_2 and $(U,Th)O_2$ showed nearly same feature. Significant two peaks were shown at ~445 cm^{-1} and at ~1150 cm^{-1}, which are assigned to U-O symmetric stretching mode in the fluorite structure and

an overtone of the first order longitudinal optical (L-O) phonon mode regarded as fingerprint for quasi-perfect fluorite structure, respectively. However, there was the defect structure due to oxygen vacancy in Raman spectra of $(U,Gd)O_{2-x}$ and $(U,Nd)O_{2-x}$ at 500 ~ 650 cm^{-1}.

For $(U,Nd)O_{2-x}$, the defect structure was clearly shown at 500 ~ 650 cm^{-1} as shown in Figure 1 (blue line). It was confirmed that this defect structure was mainly formed by oxygen vacancy. After deconvolution of Raman spectrum, the peak at ~530 cm^{-1} was ascribed as defect due to oxygen vacancy associated with Nd^{3+}. Trivalent elements replacing U^{4+} could induce the oxygen vacancy that distorts UO_2 fluorite lattice. First order L-O phonon mode due to crystal lattice distortion was observed at ~ 575 cm^{-1}. $(U,Gd)O_{2-x}$ pellet also showed similar features. On the other hand, tetravalent element Th^{4+} replacing U^{4+} had little effect on structural change of UO_2 lattice.

For $(U,Zr)O_2$, there was no defect structure related to oxygen vacancy. But distinct peak at ~598 cm^{-1} was observed as shown in Figure 1 (red line). This peak has not been observed in neither a pure ZrO_2 nor UO_2 doped with tetravalent elements other than Zr. A combined experimental-computational study found strong evidence for Zr incorporation into UO_2 fluorite structure as the $Zr-O_8$ coordinate. It was clearly shown that ZrO_8-type complex forms in the fluorite UO_2 matrix via successive accommodation of doped Zr

4. Conclusion

Lattice-doped UO_2 with various doping levels were prepared and investigated by XRD, SEM and Raman spectroscopy. Trivalent doping elements, Gd^{3+} and Nd^{3+}, formed the oxygen vacancy and the smaller grain size in UO_2 surface structure. Especially, oxygen vacancy induced defect structure reflected on Raman spectra at ~530 cm^{-1}. Tetravalent dopant, Th^{4+}, has little influence on UO_2 surface structure. However, other tetravalent dopant, Zr^{4+}, showed large influence on UO_2 surface structure. For example, distinct Raman peak at ~ about 598 cm^{-1} was observed. XRD analysis and Raman spectroscopic observation for $(U,Zr)O_2$ were consistently supported by first-principles DFT calculations. This study provides helpful information to the characterization of nuclear materials in whole nuclear fuel cycle supplying sustainable energy.

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REFERENCES

[1] H. Kleykamp, The chemical state of the fission products in oxide fuels, Journal of Nuclear Materials, Vol.131, pp. 221-246, 1985.
[2] R.J.M. Konings, T. Wiss, O. Beneš, Predicting material release during a nuclear reactor accident, Nature Materials, Vol.14, pp. 247–252, 2015.
[3] R.C. Ewing, Long-term storage of spent nuclear fuel, Nature Materials, Vol.14, pp. 252–257, 2015.
[4] M. Schmitt, J. Popp, Raman spectroscopy at the beginning of the twenty-first century, Journal of Raman Spectroscopy, Vol.37, pp. 20–28, 2006.
[5] J. Lee, J. Kim, Y.-S. Youn, N. Liu, J.-G. Kim, Y.-K. Ha, D. W. Shoemith, and J.-Y. Kim, 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, Journal of Nuclear Materials, Vol.486, pp. 216-221, 2017.
[6] J. Lee, J. Kim, Y.-S. Youn, J.-Y. Kim and S. H. Lim, Surface characterization of $(U,Nd)O_2$: the influence of trivalent-dopant on structure of UO_2, Progress in Nuclear Science and Technology Vol.5, pp. 33-36, 2018.