

Structural analysis of uranium-thorium-mixed oxides before and after oxidation using Raman spectroscopic investigation

Jeongmook Lee^{1*}, Jandee Kim¹, Young-Sang Youn¹, Sang Ho Lim^{1,2}, Jong-Yun Kim^{1,2}

¹Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 111 Daedeok-daero 989 Beon-gil, Yuseong-gu, Daejeon, Republic of Korea, 34057, *leejm@kaeri.re.kr

²Department of Radiochemistry & Nonproliferation, University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon, Republic of Korea, 34113

Uranium-thorium-mixed oxides with various compositions before and after oxidation were analyzed using Raman spectroscopy to investigate the Th doping effect on the structural changes and oxidation behavior of UO₂. The results indicate that Th affects the oxidation of UO₂ because the oxygen-to-metal ratio of oxidized uranium-thorium-mixed oxides decreases with an increase in Th content under the same oxidation conditions. A Raman spectra analysis showed that the Th doping effect induced crystal lattice disorder of UO₂ matrix during oxidation.

I. Introduction

Fission products including actinides, lanthanides, trans-uranium elements and activation products are produced and located in spent UO₂ nuclear fuel after irradiation.^{1,2} Among them, certain metal (M) atoms are doped in nuclear fuel such as M-doped UO₂ form.² Depending on the doped metal, the structural characteristic of the UO₂ matrix and the oxidation state of uranium can change considerably.³ The metal doping effect also has a large influence on the oxidation kinetics of UO₂. Although there are significant differences in the air oxidation behavior between unirradiated and spent UO₂ fuel,⁴ it was suggested that a doped metal can modify the oxidation kinetics of the spent fuel.⁵

A simple simulated spent fuel such as single-metal-doped UO₂ has been studied using Raman spectroscopy to understand the doping effect on the UO₂ structure and the structural characteristic of spent nuclear fuel. For example, the defects and oxygen stoichiometry in unirradiated uranium oxides⁶ and the La doping effect on the oxidation kinetics of UO₂ fuel materials⁷ were recently investigated in detail using Raman spectroscopy. We have previously reported the effect of a trivalent dopant, Gd³⁺, on the UO₂ structure using Raman spectroscopy.⁸

In this study, a structural analysis of uranium-thorium-mixed oxides before and after oxidation was investigated using Raman spectroscopy to identify the effects of a tetravalent dopant on the structure and oxidation behavior of UO₂.

II. Experimental Procedure

Th-doped UO₂ sample pellets with various doping levels (1, 5, 10 mol%) were prepared using a solid-state reaction with powder mixing. UO₂ and ThO₂ powders were blended using an agate mortar. The powder mixtures were compressed into a disk-shaped pellet form. The pressed pellets were sintered at 1700 °C for 18 h in a hydrogen atmosphere to avoid the formation of oxidized forms of uranium dioxide. The sintered pellets were annealed in the same atmosphere at 1200 °C for 12 h, and then cooled to room temperature in flowing hydrogen gas. An undoped UO₂ pellet was also prepared using the same procedure. The oxidation of the pure and Th-doped UO₂ pellets was conducted at CO/CO₂ = 0.1 for 24 h.

X-ray diffraction (XRD) data of each sample were obtained using a Bruker D8 Advance at room temperature. The lattice parameters of the samples were calculated from the refinement process. Raman spectra of each pellet were acquired using an ANDOR Shamrock SR500i spectrometer with a 633nm wavelength He-Ne laser. 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.

III. Results and Discussion

The lattice parameter of the prepared samples before oxidation increased almost linearly with the increase in Th content. This linear relationship indicates that Th was well dissolved in a UO₂ matrix with the remaining fluorite structure.⁹ After oxidation, the lattice parameter decreased for the same Th content because of the contraction of lattice owing to the accommodation of O interstitial ions and the creation of the smaller U⁵⁺(0.86 Å) than U⁴⁺(1.05 Å).⁶

Oxygen-to-metal (O/M) ratios of the oxidized sample were calculated from the weight gains, whereas the oxidation at CO/CO₂ = 0.1 assumes that the samples prepared under a hydrogen atmosphere are stoichiometric oxides. It was confirmed that the O/M ratio of the oxidized samples decreased with an increasing Th doping level under same oxidation conditions.

Raman spectra of Th-doped UO₂ showed a nearly similar feature with that of undoped UO₂. Compared to the Raman spectra of Gd-doped UO₂,⁸ there is no defect structure in those of Th-doped UO₂. For the replacement from U⁴⁺ to Th⁴⁺, the creation of a significant number of oxygen vacancies is not required to compensate for a charge imbalance. For the oxidized samples, a defect structure was observed within 500-650 cm⁻¹ in the Raman spectra. In particular, the relative intensity of the peak at ~570 cm⁻¹ to T_{2g} main peak at ~445 cm⁻¹ increased with the increase in Th content. This feature indicates that crystal lattice disorder of the fluorite structure during oxidation increased as the Th doping level increased because the peak at ~570 cm⁻¹ has been assigned to the first-order longitudinal optical phonon, which arises owing to crystal lattice disorder.¹⁰

IV. Conclusions

Uranium-thorium-mixed oxide sample pellets with various doping levels (1, 5, 10 mol%) before and after oxidation have been analyzed using XRD and Raman spectroscopy techniques. The lattice contraction and O/M ratios of the samples after oxidation were obtained. Th had an effect on the oxidation of the sample pellets. In the compared Raman spectra of the sample after oxidation and before oxidation, the Th doping effect induced a crystal lattice disorder during oxidation.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science, ICT and Future Planning, MSIP)

REFERENCES

1. R. J. M. Konings, T. Wiss and O. Beneš, "Predicting material release during a nuclear reactor accident," *Nat. Mater.*, **14**, 247 (2015).
2. R. C. Ewing, "Long-term storage of spent nuclear fuel," *Nat. Mater.*, **14**, 252 (2015).
3. S. M. Ho and K. C. Radford, "Structural chemistry of solid solutions in UO₂-Gd₂O₃ system," *Nucl. Technol.*, **73**, 350 (1986).
4. L. E. Thomas, R. E. Einziger and H. C. Buchanan, "Effect of fission products on, air-oxidation of LWR spent fuel," *J. Nucl. Mater.*, **201**, 310 (1993).
5. J.-W. Choi, R. J. McEachern, P. Taylor and D. D. Wood, "The effect of rare-earth fission products on the rate of U₃O₈ formation on UO₂," *J. Nucl. Mater.*, **230**, 250 (1996).
6. H. He and D. Shoesmith, "Raman spectroscopic studies of defect structures and phase transition in hyper-stoichiometric UO_(2+x)," *Phys. Chem. Chem. Phys.*, **12**, 8108 (2010).
7. Z. Talip, T. Wiss, P.E. Raison, J. Paillier, D. Manara, J. Somers and R. J. M. Konings, "Raman and X-ray studies of uranium-lanthanum-mixed oxides before and after air oxidation," *J. Am. Ceram. Soc.*, **98**, 2278 (2015).
8. J. Lee, J. Kim, Y.-S. Youn, N. Liu, J.-G. Kim, Y.-K. Ha, D. W. Shoesmith 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," *J. Nucl. Mater.*, **486**, 216 (2017).
9. Y.-K. Ha, J.-G. Kim, Y.-J. Park and W.-H. Kim, "Effect of a tetravalent dopant, Th⁴⁺ on the oxidation of uranium dioxide," *Key Eng. Mater.*, **277-279**, 654 (2005)
10. T. Livneh and E. Sterer, "Effect of pressure on the resonant multiphonon Raman scattering in UO₂," *Phys. Rev. B.*, **73**, 085118 (2006).