Korea Atomic Energy Research Institute

Experimental Characterization and First-Principles Understanding on the Structure of Zr-doped UO_2

15th November 2019

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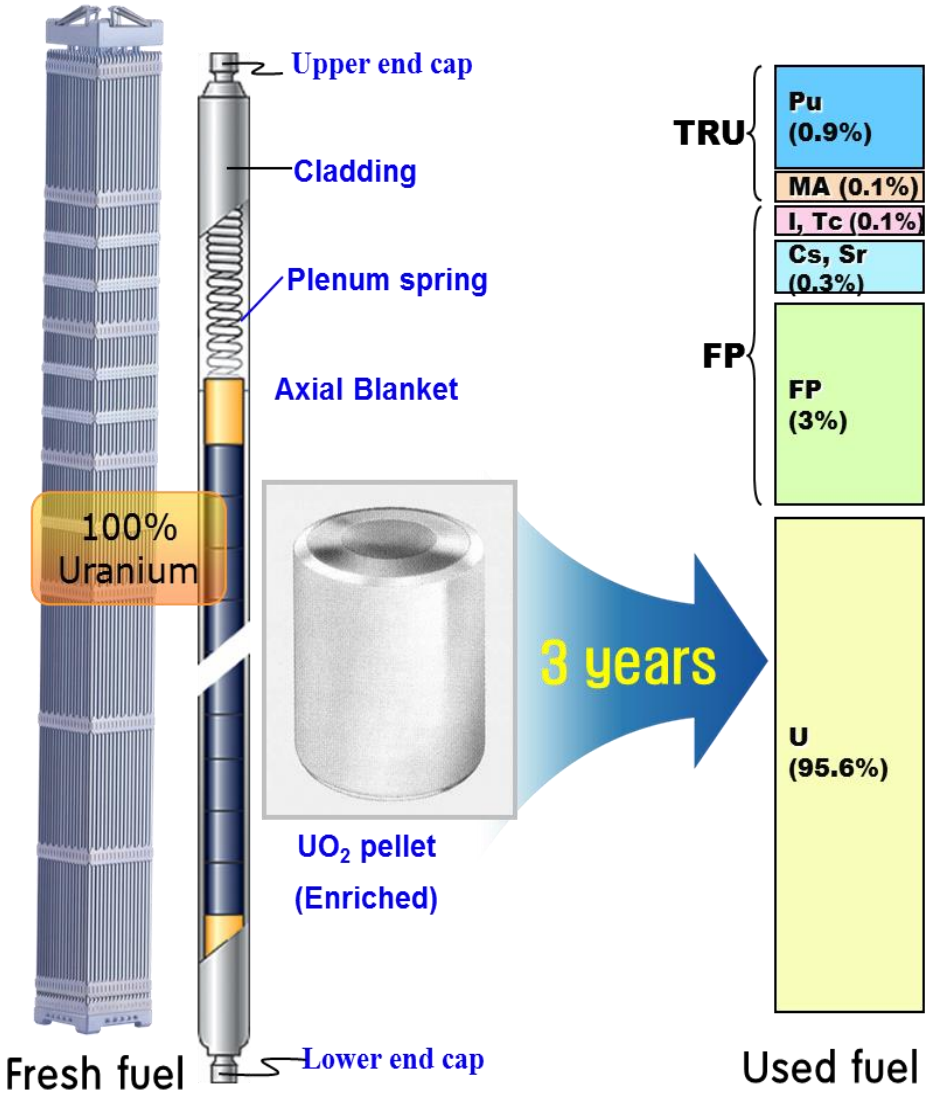
I. Introduction

I. Introduction

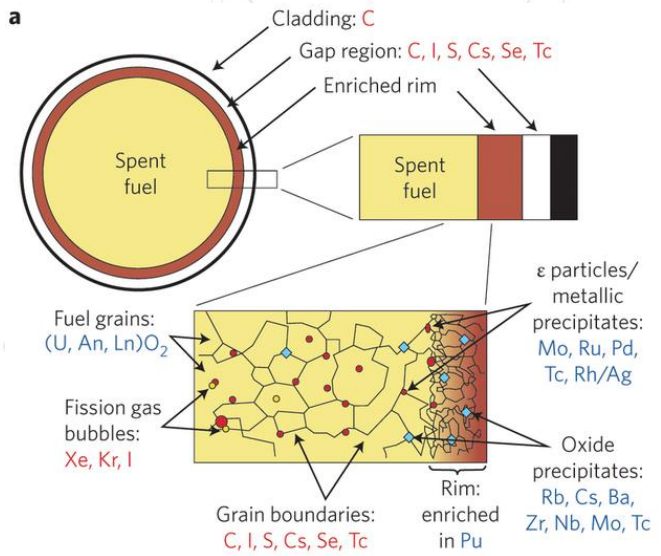
Distribution of fission products and actinides after irradiation



Chemical inventory for HBU SNF in CORE and OUT regions.

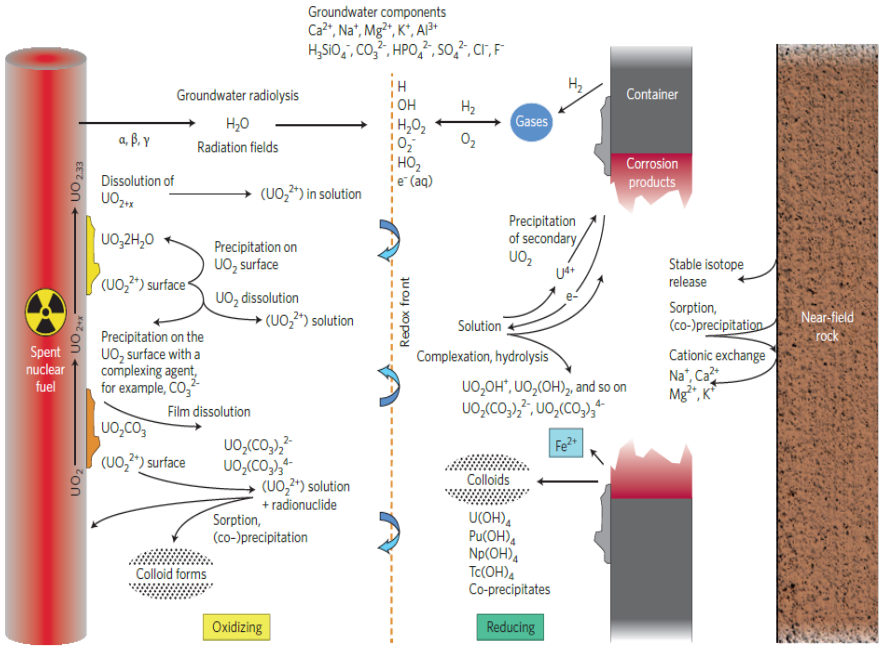
Element	HBU-CORE (μg/g)	HBU-OUT (μg/g)
Rb	500 ± 100	600 ± 120
Sr	800 ± 160	800 ± 160
Y	310 ± 130	340 ± 150
Zr	6300 ± 1300	7900 ± 1600
Mo	5900 ± 1180	8000 ± 1600
Tc	1300 ± 260	1600 ± 300
Ru	4400 ± 880	5300 ± 1100
Rh	650 ± 130	800 ± 160
Cs	3800 ± 200	4800 ± 240
La	2000 ± 400	2300 ± 500
Nd	7000 ± 1400	8000 ± 1600
U	780000 ± 78000	770000 ± 77000
Np	810 ± 160	760 ± 150
Pu	8000 ± 1600	11000 ± 2200
Am	840 ± 170	1200 ± 240
Cm	290 ± 60	460 ± 90

D. Serrano-Purroy *et al.*, J. Nucl. Mater. 427 (2012) 249-258



R.C. Ewing, Nature Mater. 14 (2015) 252-257
J. Bruno *et al.*, Elements 2 (2006) 343-349

I. Introduction



Component (fission products, actinides, burn-up)
Physical properties (structure, thermal conductivity)
Chemical Properties (chemical state, oxidation, reactivity)

Doping effect → **Structural change & Reactivity**

Complex material, Spent Nuclear Fuel ⟷ **Simplified single-element-doped UO_2**

Zr^{4+}

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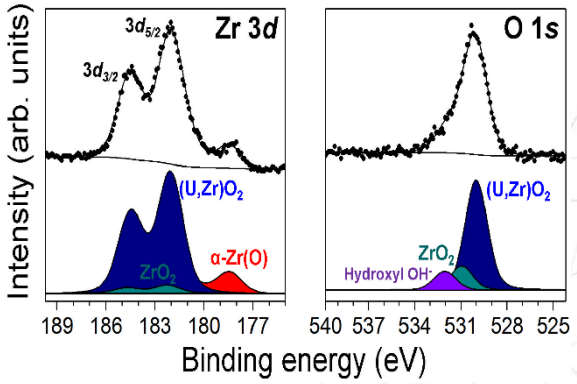
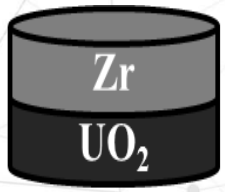


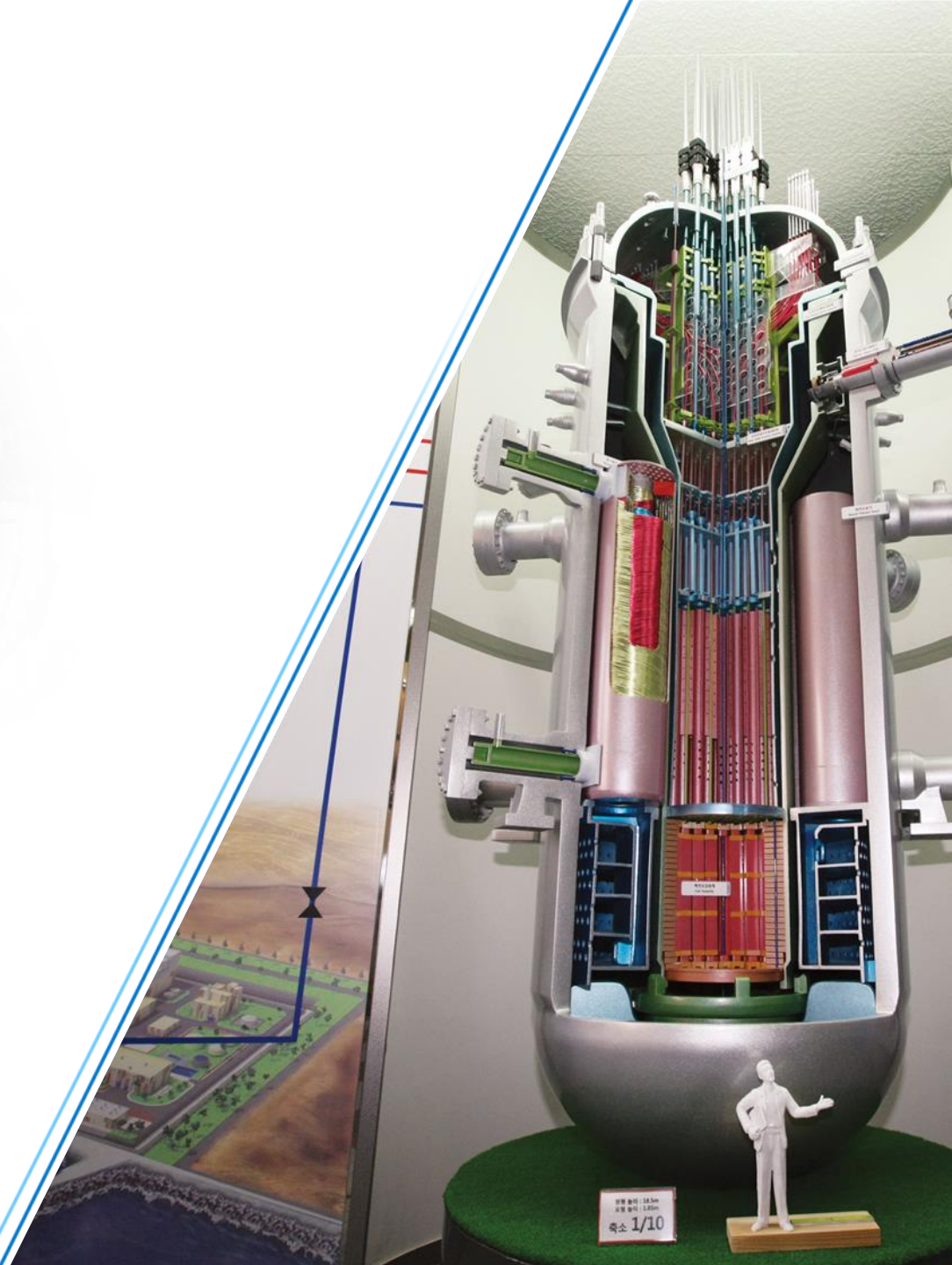


UO_2-Zr sample

Y.-S. Youn *et al.*, Bull. Korean Chem. Soc. 36 (2015) 2068-2072

R.C. Ewing, Nature Mater. 14 (2015) 252-257
B. Grambow *et al., Source Term for Performance Assessment of Spent Fuel as a Waste Form EUR19140 Report* 1–355 (Euratom, 2000).

II. Experiment



II. Experiment

Preparation of pellet

Powder mixing of UO_2 and ThO_2 powder

$U^{4+}O_2^{2-}$, $Zr^{4+}O_2^{2-}$

↓

Pressed into a disk pellet

↓

Sintering at 1700ºC for 18 h in a reducing atmosphere with flowing hydrogen

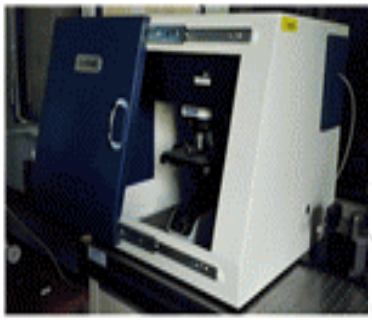
$$\mathbf{U_{1-y}^{4+}Zr_y^{4+}O_2^{2-}}$$

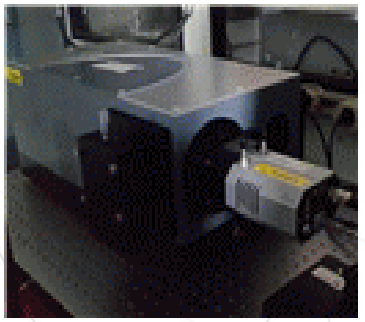
Thickness : < 1 mm
Diameter: ~ 9 mm

XRD (X-Ray Diffraction)

Bruker AXS D8 Advance X-ray Diffractometer using CuKα radiation at room temperature

Raman spectroscopy





ANDOR Shamrock SR500i spectrometer with a 632.8 nm excitation of He-Ne laser

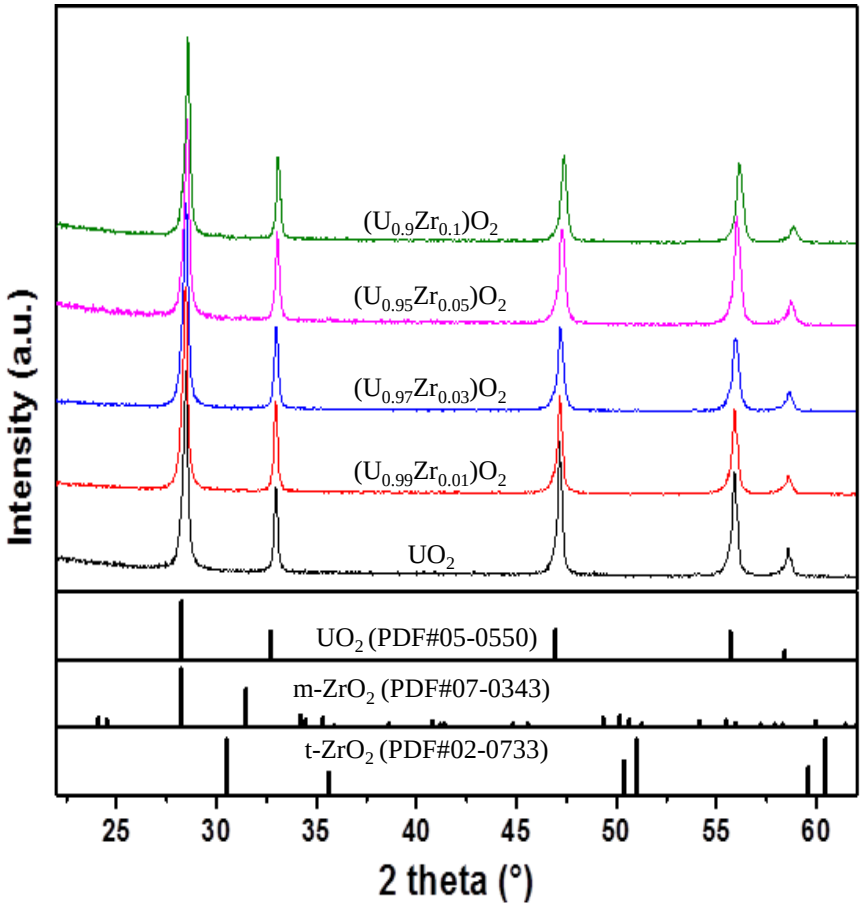
First-principles DFT calculations

-DFT implemented in VASP
-The projector-augmented wave (PAW) method :
represent the core electrons
-The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE):
correct the exchange and correlation potentials
-Energy cut-off of 600 eV were used for all calculations

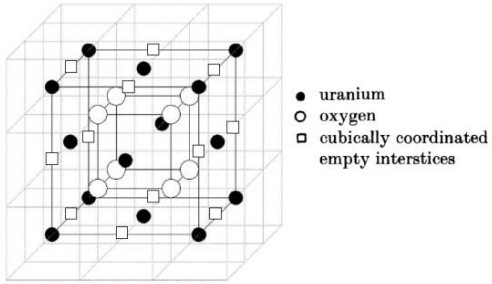
III. Results & Discussion

III. Results & Discussion

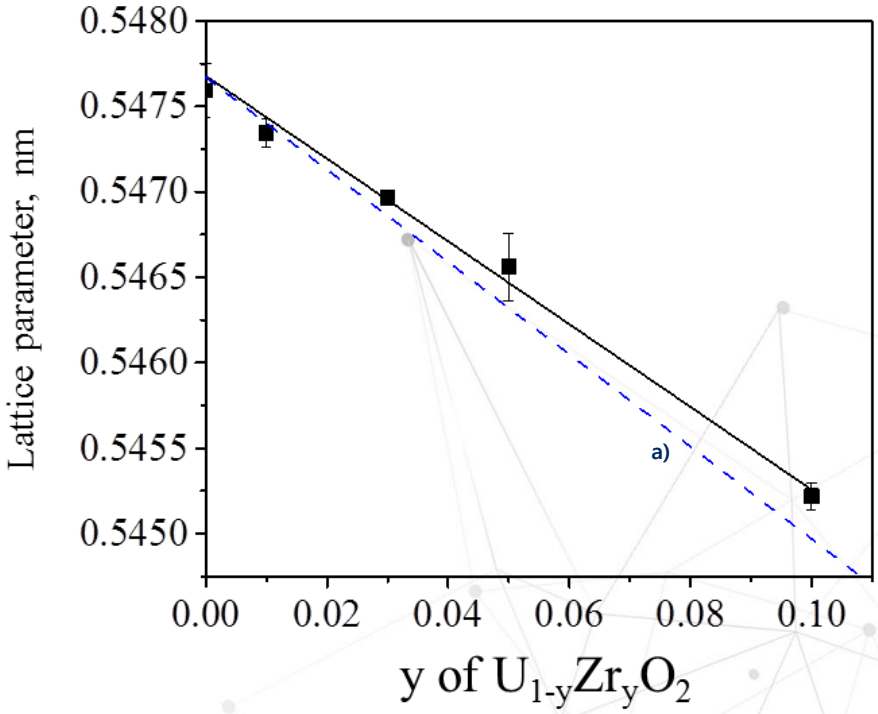
XRD data of $(U,Zr)O_2$



m : monoclinic, t : tetragonal



Ionic radius
U^{4+} : 0.1001 nm
Zr^{4+} : 0.084 nm

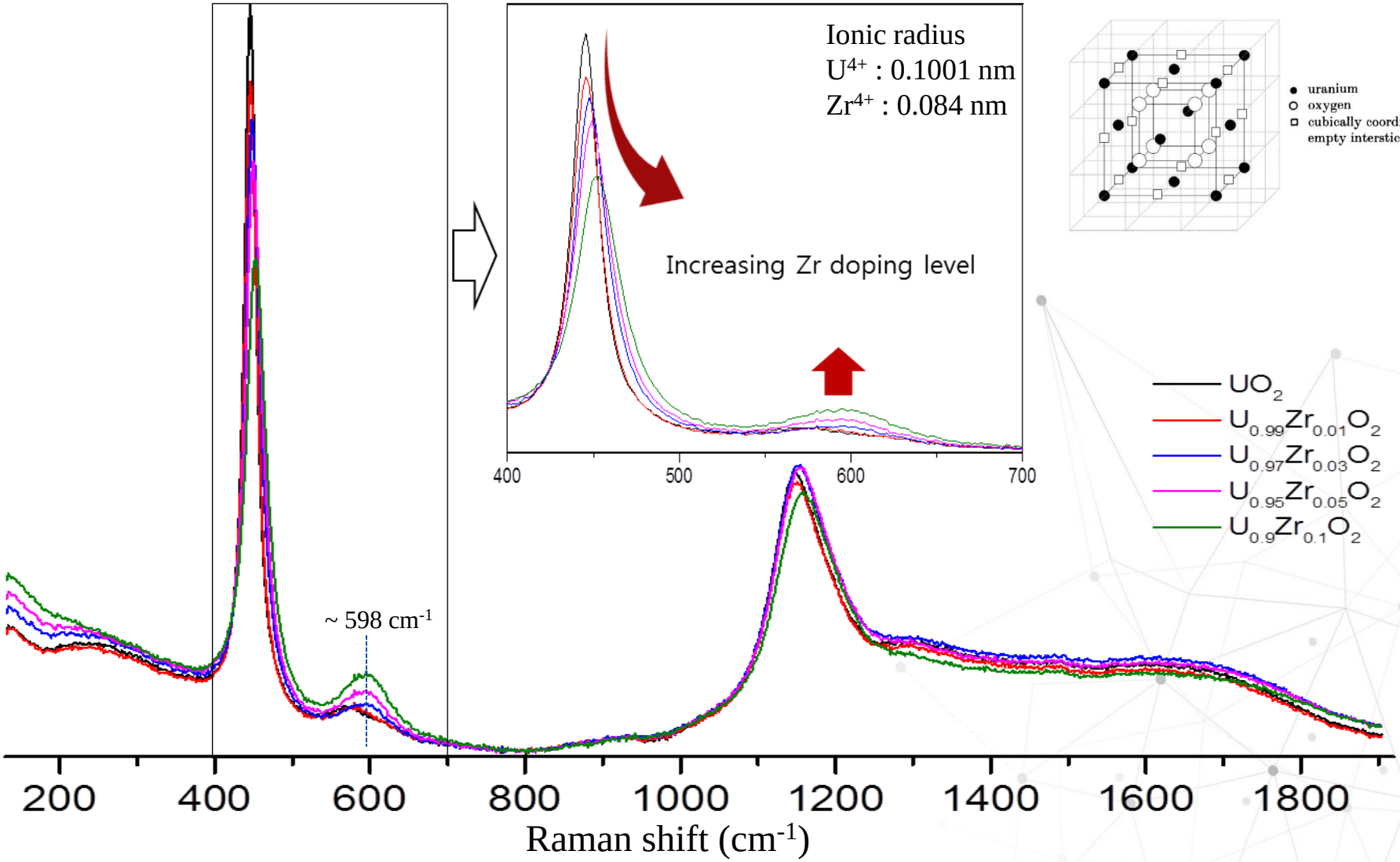


[a] **K. Une** *et al.*, J. Am. Ceram. Soc. 66 (1983) C179-C180

J. Lee *et al.*, Int. J. Energy Res. 43 (2019) 3322-2229

III. Results & Discussion

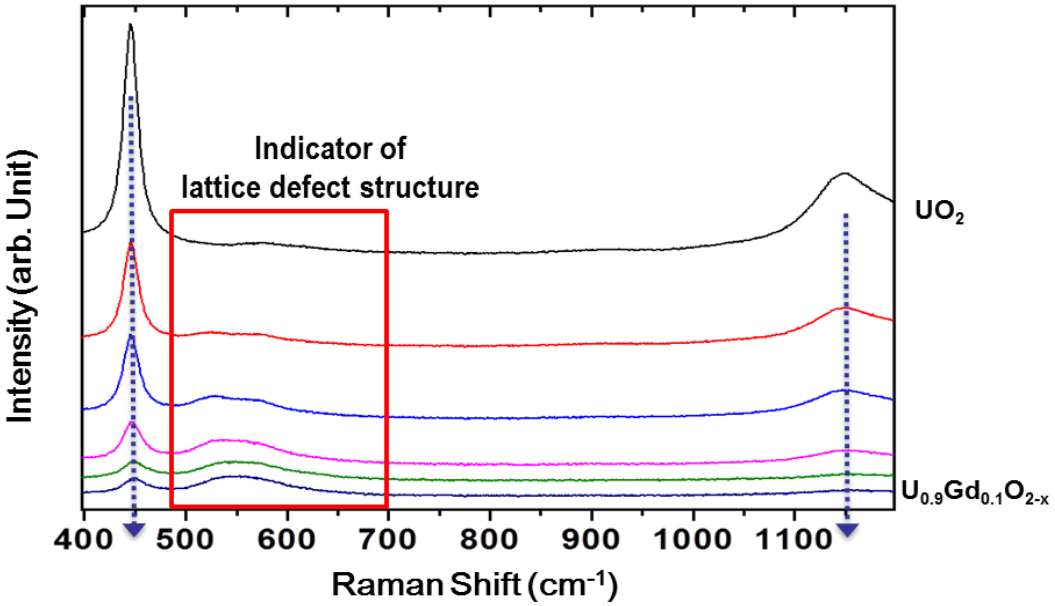
Raman spectra of $(U,Zr)O_2$

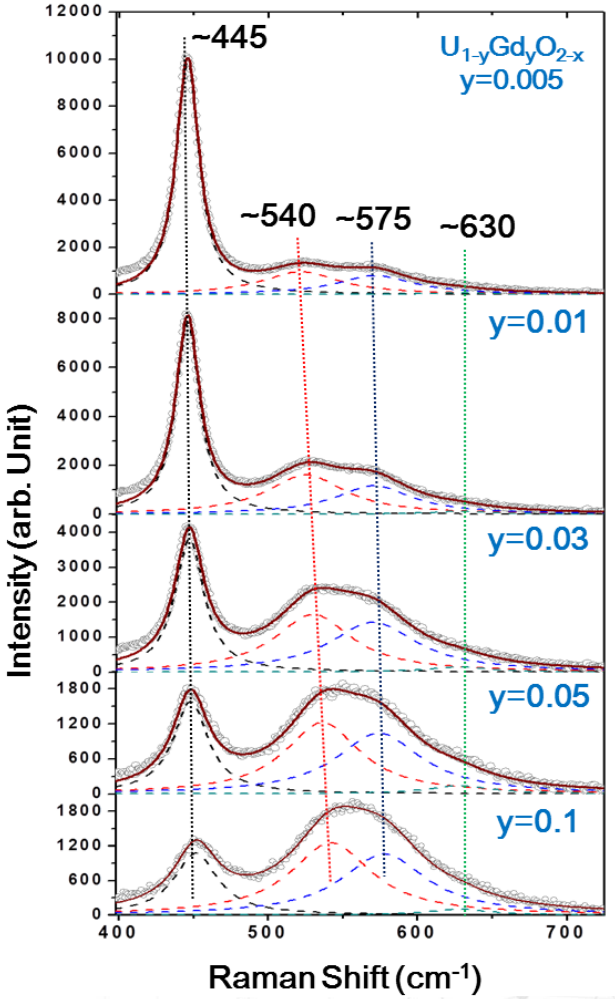


J. Lee *et al.*, Int. J. Energy Res. 43 (2019) 3322-2229

III. Results & Discussion

Raman spectra of $(U,Gd)O_2$



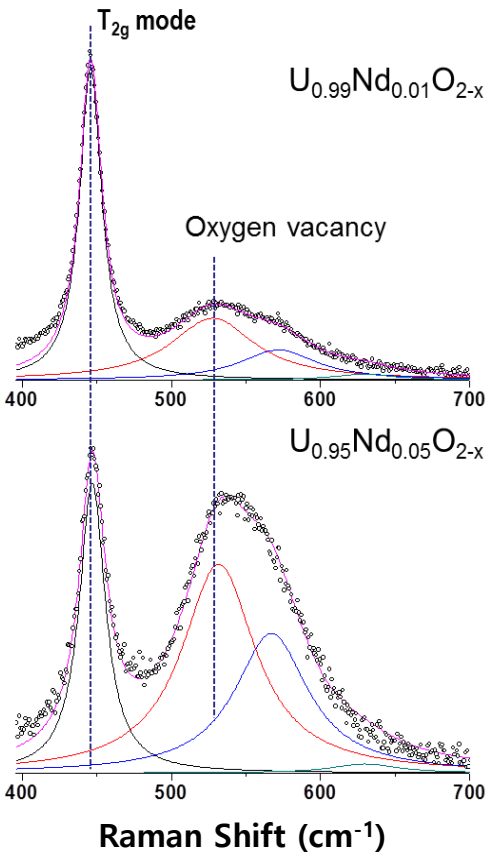


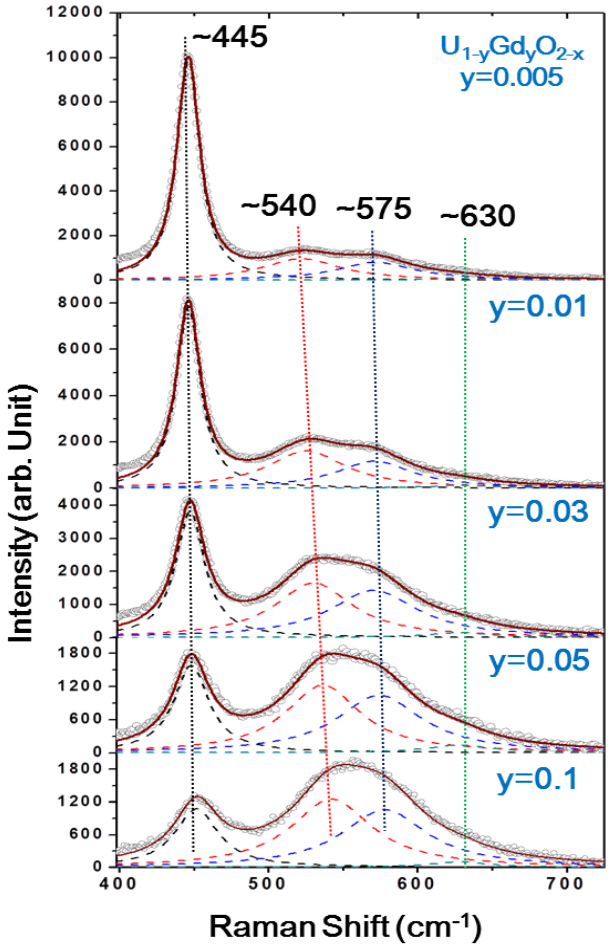
~445 cm^{-1} : T_{2g} fundamental O-U stretch at perfect fluorite structure
~540 cm^{-1} : Lattice distortion from creation of oxygen vacancies due to Gd^{3+}
~575 cm^{-1} : L-O (Longitudinal-Optical) phonon band
~630 cm^{-1} : Cuboctahedral constituting of the U_4O_9 phase
~1150 cm^{-1} : 2 L-O phonon

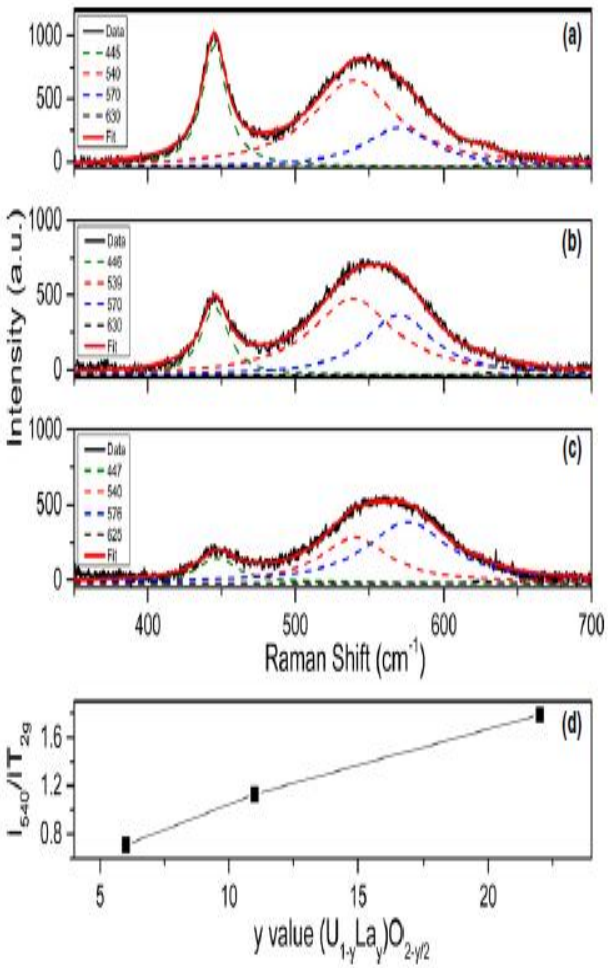
J. Lee *et al.*, J. Nucl. Mater. 486 (2017) 216-221

III. Results & Discussion

Compare with other results







Ln^{3+} doping elements show similar features

y = 0.06, 0.11, and 0.22 in $U^{4+}_{1-y}La^{3+}_{y}O^{2-}_{2-y/2}$

J. Lee *et al.*, Prog. Nucl. Sci. Technol. 5 (2018) 33-36

J. Lee *et al.*, J. Nucl. Mater. 486 (2017) 216-221

Z. Talip *et al.*, J. Am. Ceram. Soc. 98 (2015) 2278-2285

III. Results & Discussion

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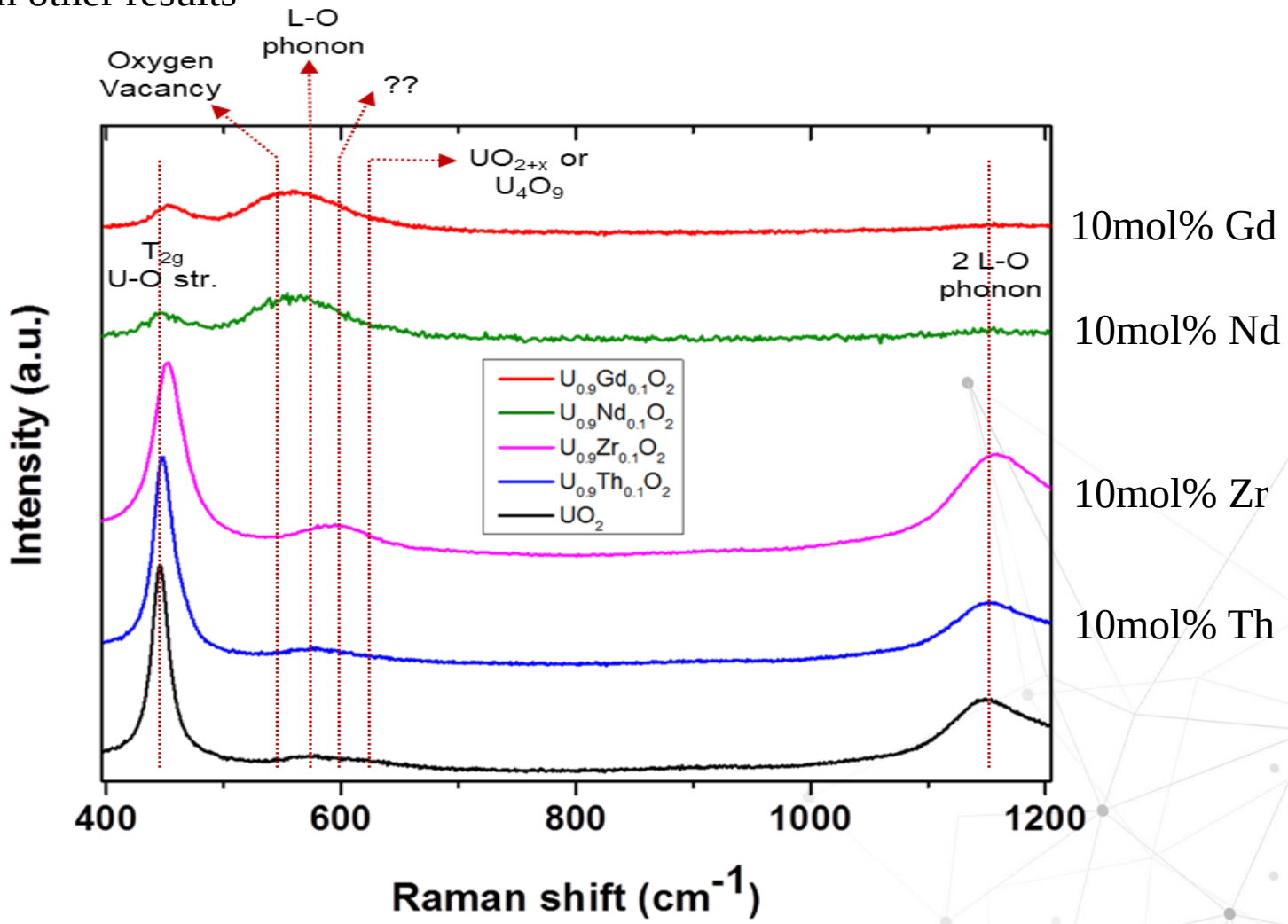

J. Lee *et al.*, J. Nucl. Mater. 486 (2017) 216-221
J. Lee *et al.*, Prog. Nucl. Sci. Technol. 5 (2018) 33-36
J. Lee *et al.*, Int. J. Energy Res. 43 (2019) 3322-2229
J. Lee *et al.*, J. Radioanal. Nucl. Chem. 316 (2018) 1295-1300

III. Results & Discussion

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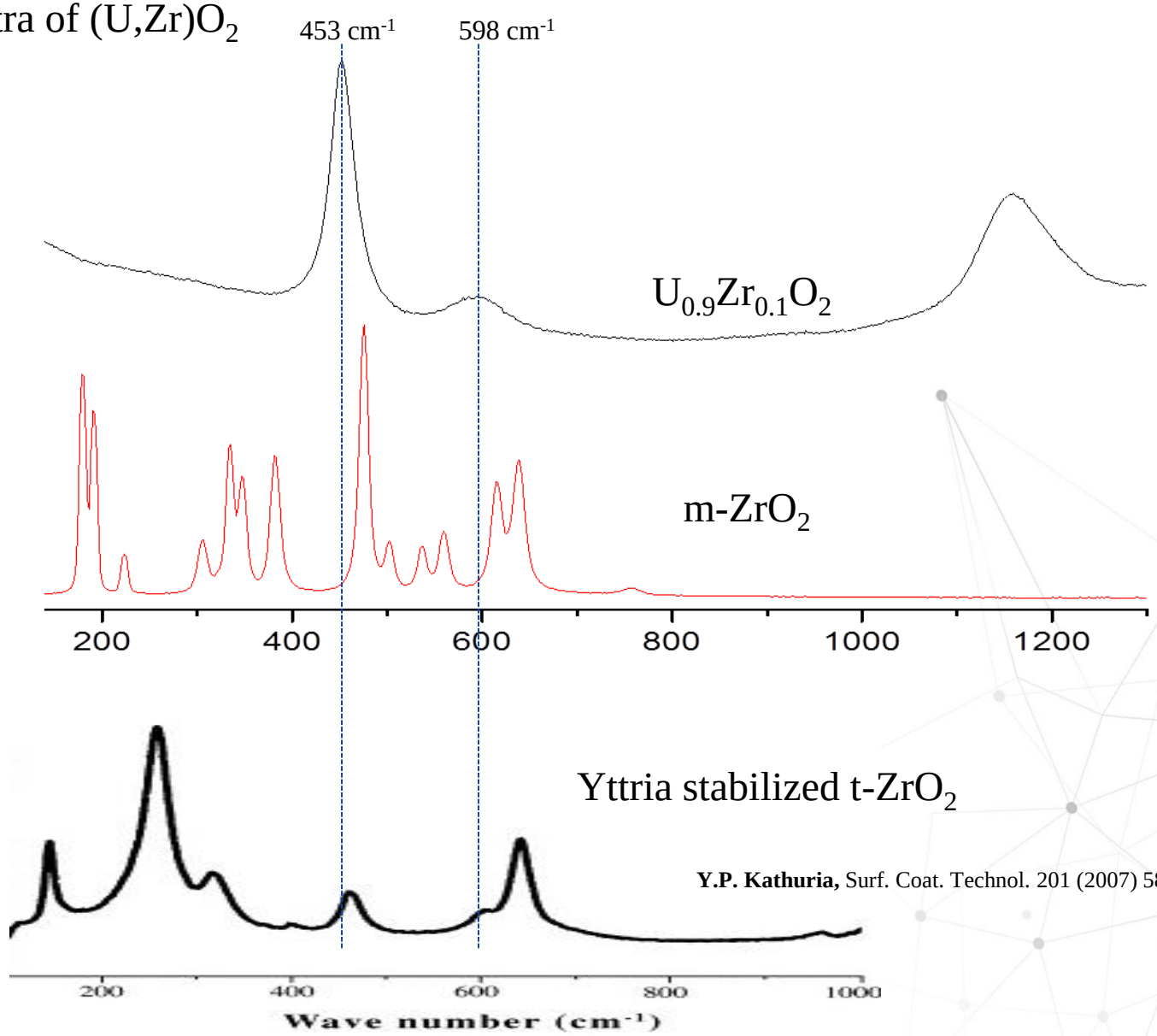

Y.P. Kathuria, Surf. Coat. Technol. 201 (2007) 5865-5869

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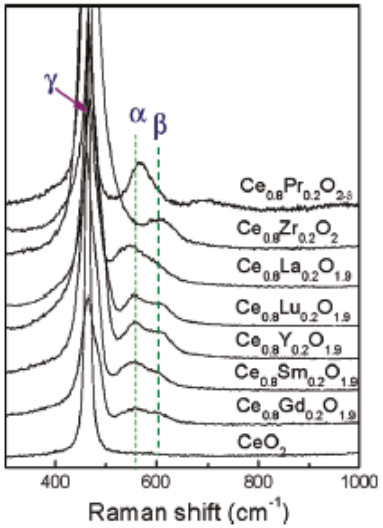

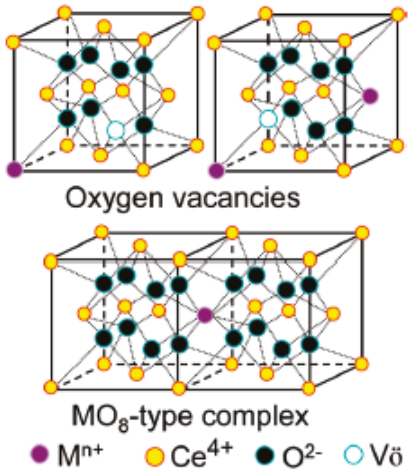

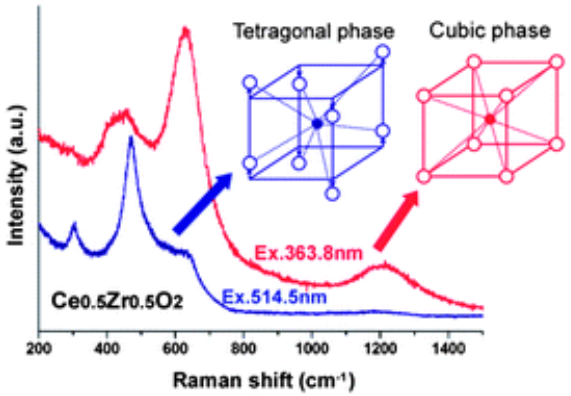

T. Taniguchi *et al.*, Nanoscale 2 (2010) 1426-1428

L. Li *et al.*, J. Phys. Chem. A 115 (2011) 7972-7977

J. Lee *et al.*, Int. J. Energy Res. 43 (2019) 3322-2229

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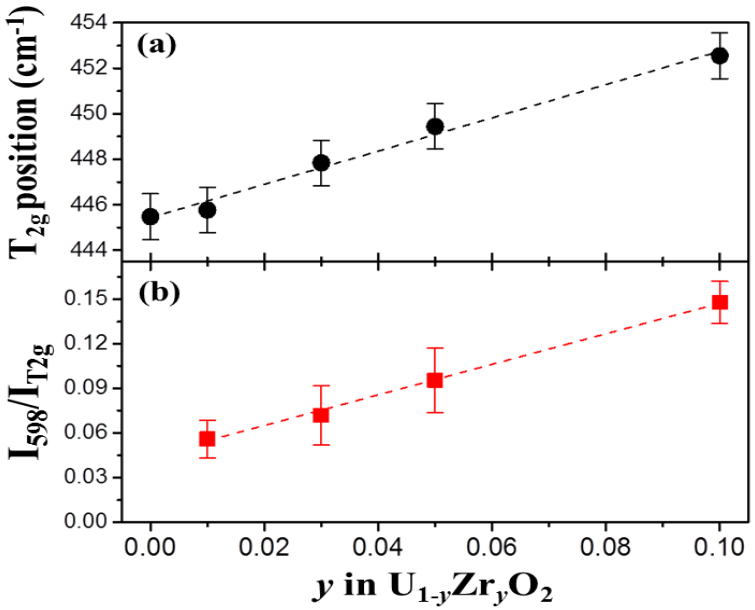

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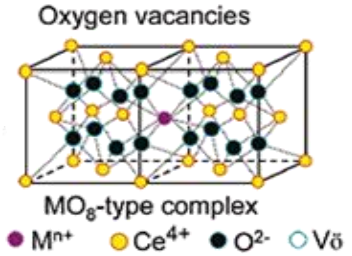
III. Results & Discussion

First-principles DFT calculations



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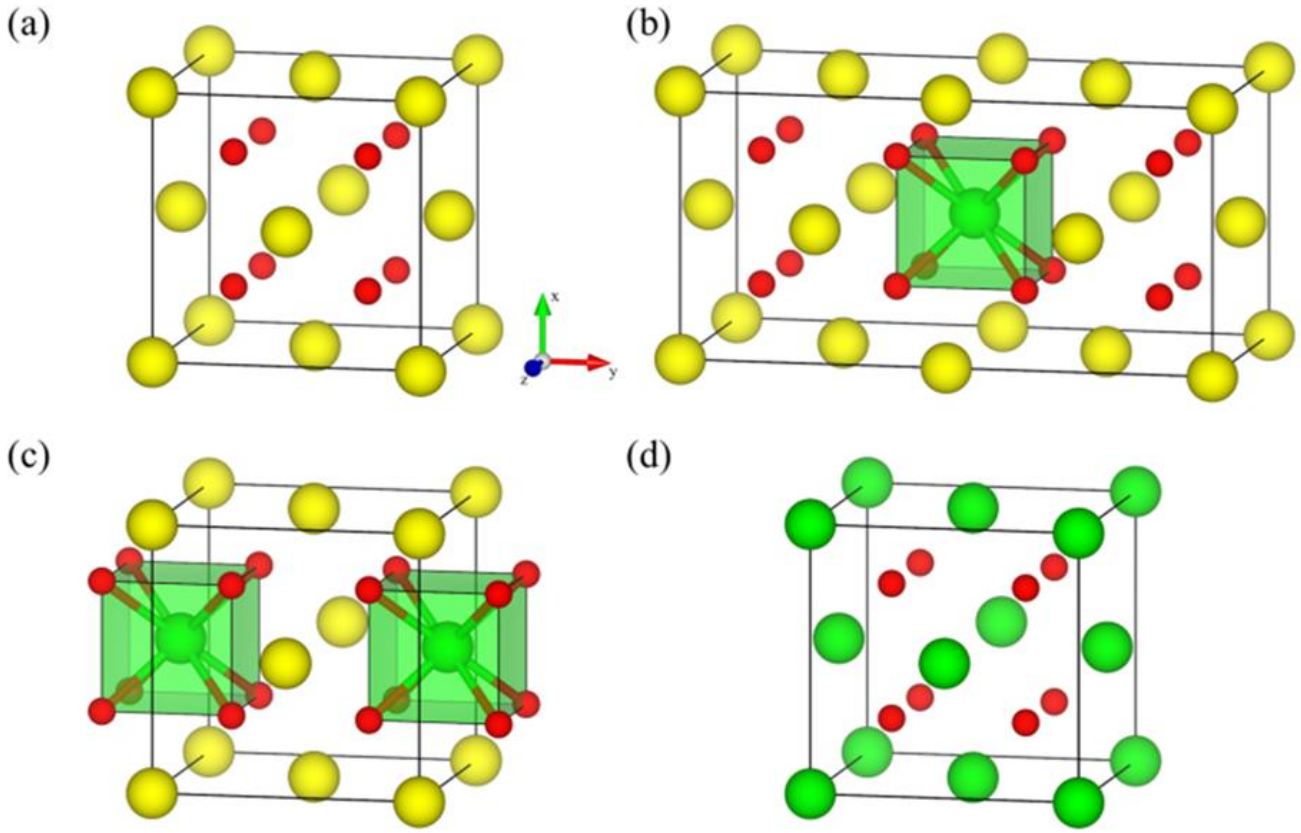

Model systems of (a) UO_2, (b) $U_{0.87}Zr_{0.13}O_2$, (c) $U_{0.75}Zr_{0.25}O_2$, and (d) cubic ZrO_2. The yellow, green, and red spheres represent U, Zr, and O atoms, respectively

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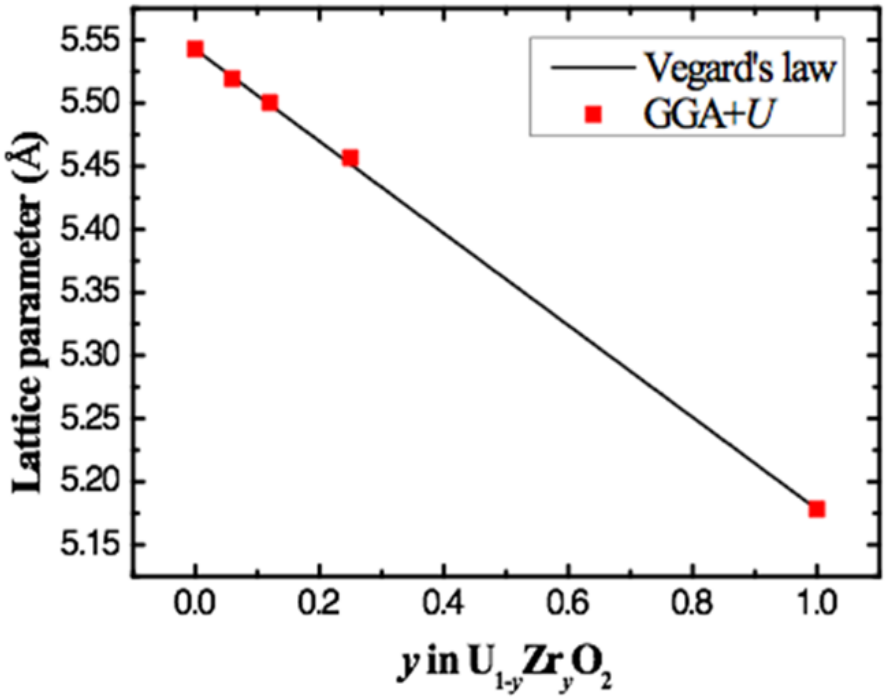
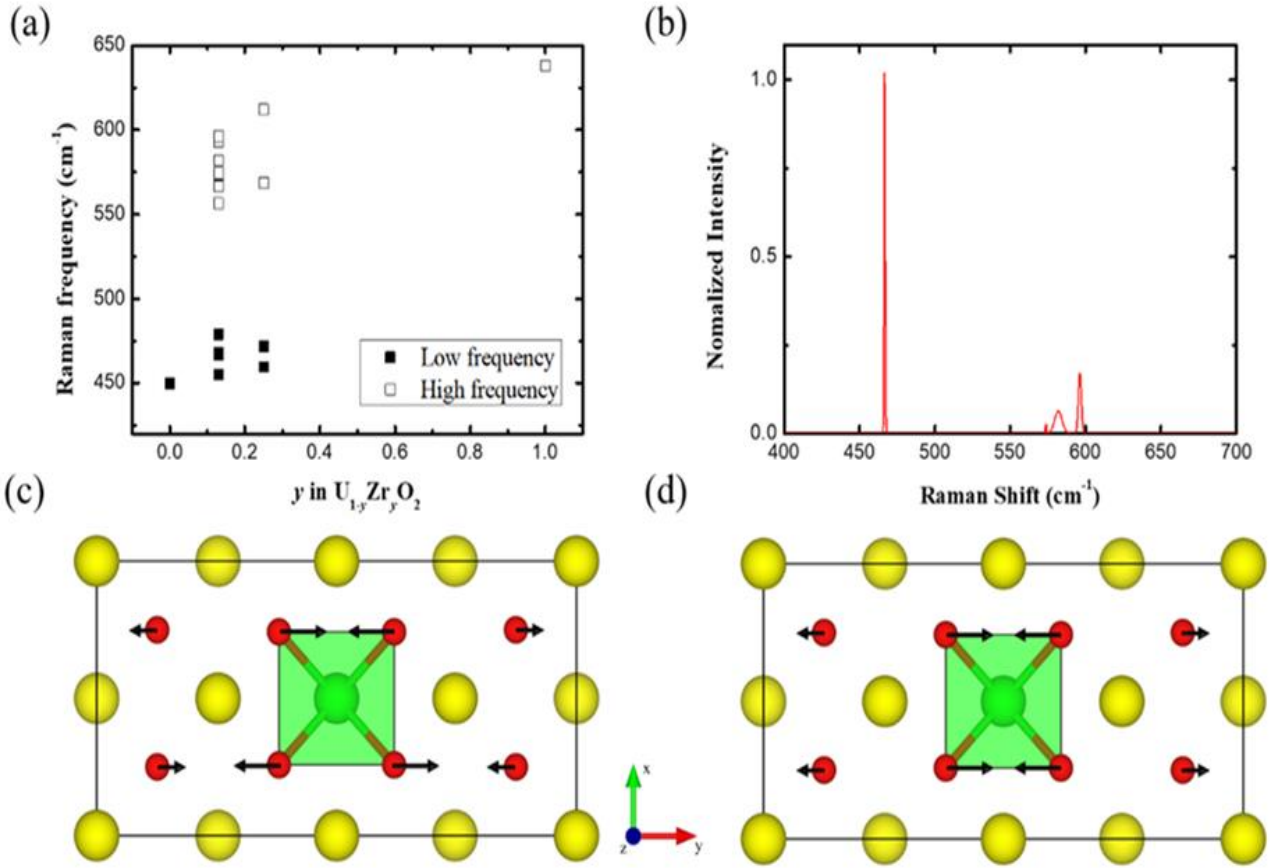


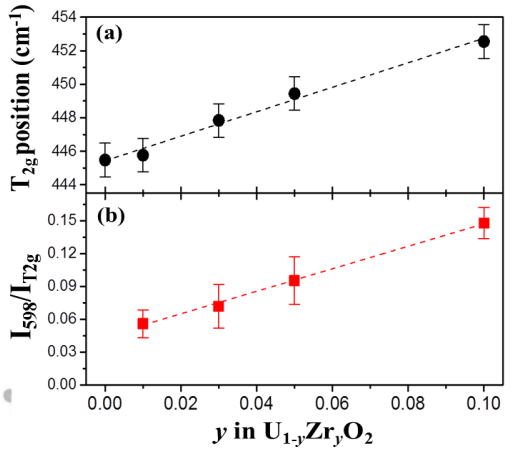
Relationship between the simulated lattice parameter (red squares) calculated using GGA+*U* and Zr content (*y*) in $U_{1-y}Zr_yO_2$ (*y* = 0.0, 0.06, 0.13, 0.25, and 1). This linear relationship obeys Vegard's law (solid black line).

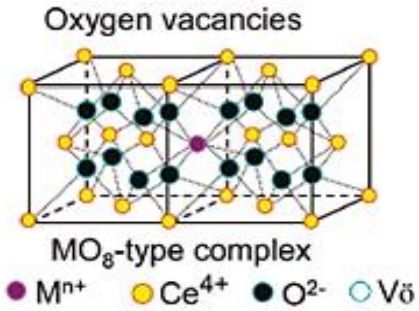
J. Lee *et al.*, Int. J. Energy Res. 43 (2019) 3322-2229

III. Results & Discussion

First-principles DFT calculations







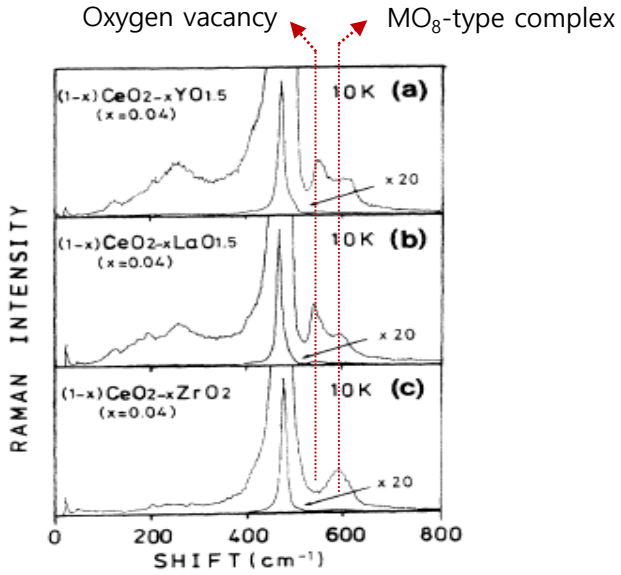
Ionic radius
U^{4+} : 0.1001 nm
Zr^{4+} : 0.084 nm

(a) Vibrational frequencies of $U_{1-y}Zr_yO_2$ as a function of Zr composition (*y*). (b) The simulated intensities and Raman frequencies of $U_{0.87}Zr_{0.13}O_2$. Normal modes of the peaks at (c) 466.82 cm^{-1} and (d) 596.15 cm^{-1}. The yellow, green and red spheres represent U, Zr and O atoms, respectively.

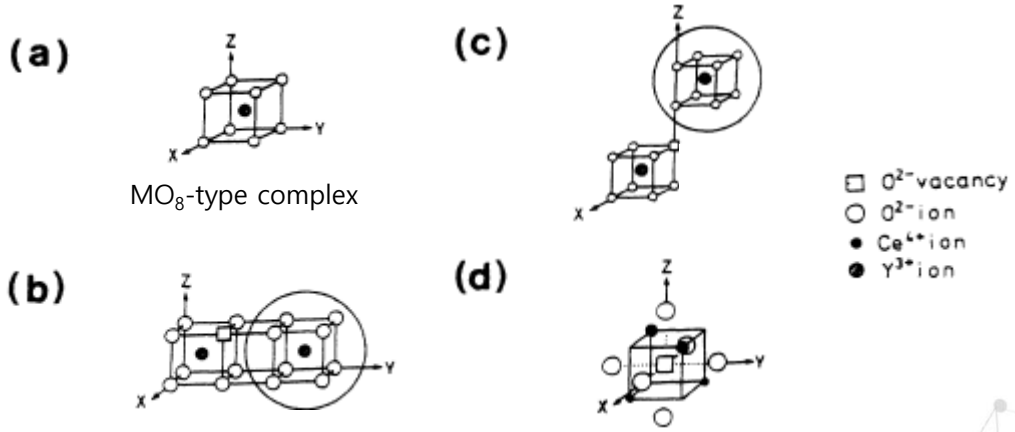
J. Lee *et al.*, Int. J. Energy Res. 43 (2019) 3322-2229

III. Results & Discussion

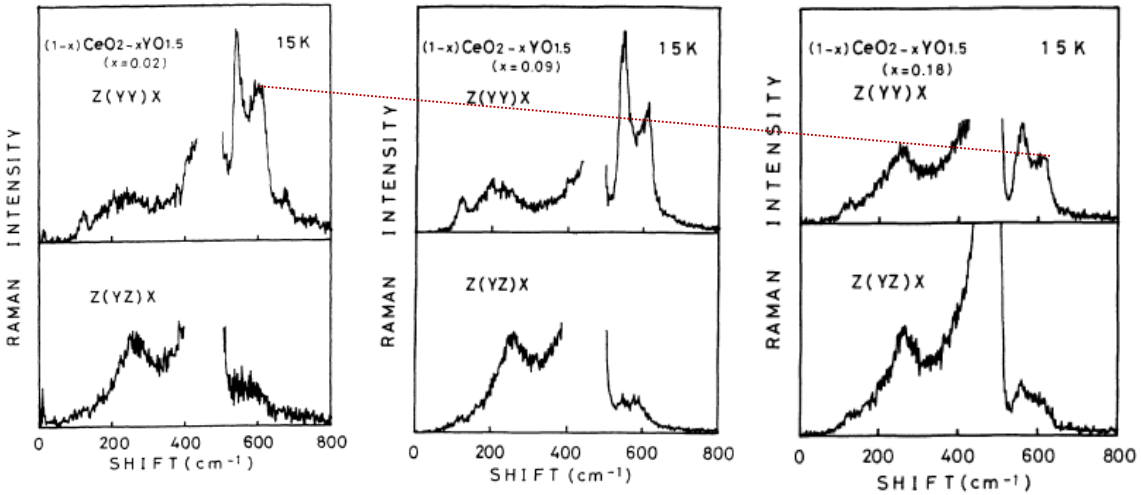
How about M(III)O_8-type complex?



$(Ce,Y)O_2$



(b), (c), (d) Defect spaces related to oxygen vacancy



The existence of a MO_8-type complex :

Dopant M is in 8-fold coordination with O^{2-} (O_h symmetry) excluding oxygen vacancy

Increasing the concentration of Ov :

the space differs from the MO_8-type complex since the space no longer has O_h symmetry due to the effect of the neighboring oxygen vacancy.

A. Nakajima *et al.*, Phys. Rev. B 50 (1994) 13297-13307

IV. Summary

IV. Summary

Summary

- The surface structure of $U_{1-y}Zr_yO_2$ pellets have been studied by XRD and Raman spectroscopy
- There is no defect structure related to oxygen vacancy
- The peak at ~ 598 cm^{-1} in $U_{1-y}Zr_yO_2$ pellet is supposed to be the existence of ZrO_8-type complex in UO_2 matrix.
- T_{2g} Raman vibration peak around 445 cm^{-1} shows positive shift and the I_{598}/I_{T2g} linearly increases with increasing Zr doping level
- XRD analysis and Raman spectroscopic observation was consistently supported by first-principles DFT calculation (O in the ZrO_8-type complex moves longer distance)
- This study could provide important implication for predicting physicochemical properties of a corium (the mixture of core materials, UO_2 and ZrO_2) and reaction product of fuel and cladding

Ongoing and future work

- Electrochemical experiments with $(U,Zr)O_2$
- Experimental characterization integrated with first-principles computational validation on the surface structure of $(U,M^{3+})O_2$

Thank you!