

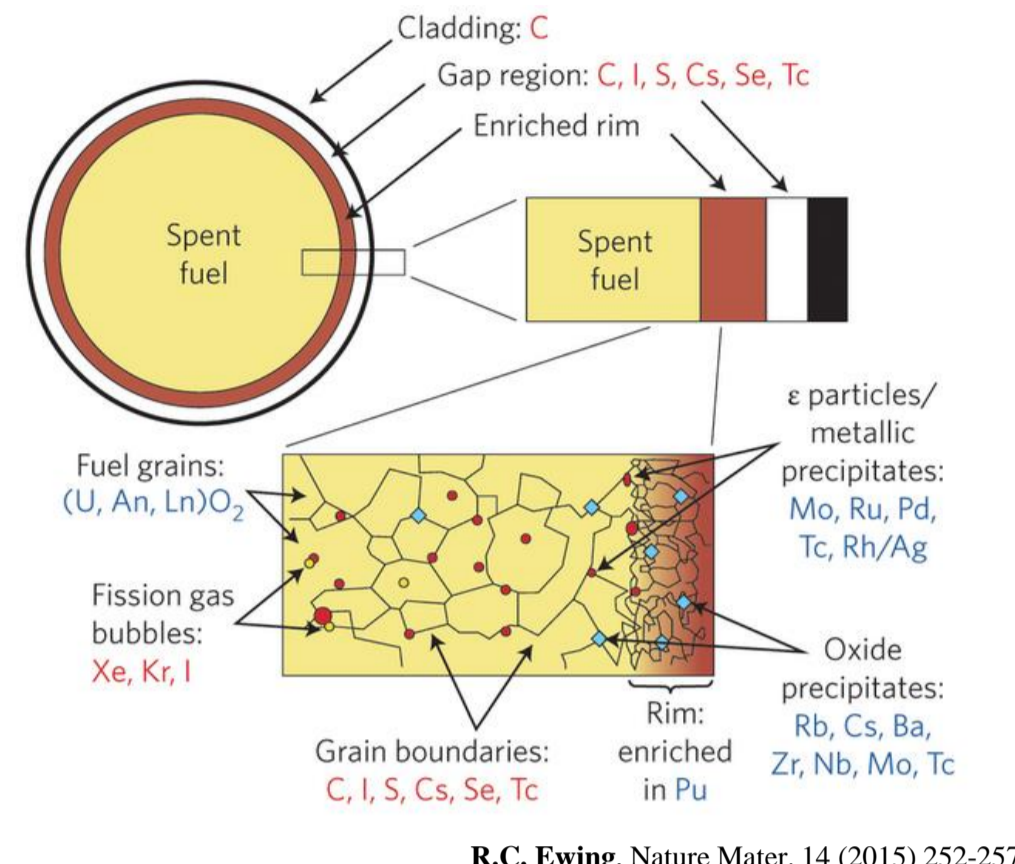
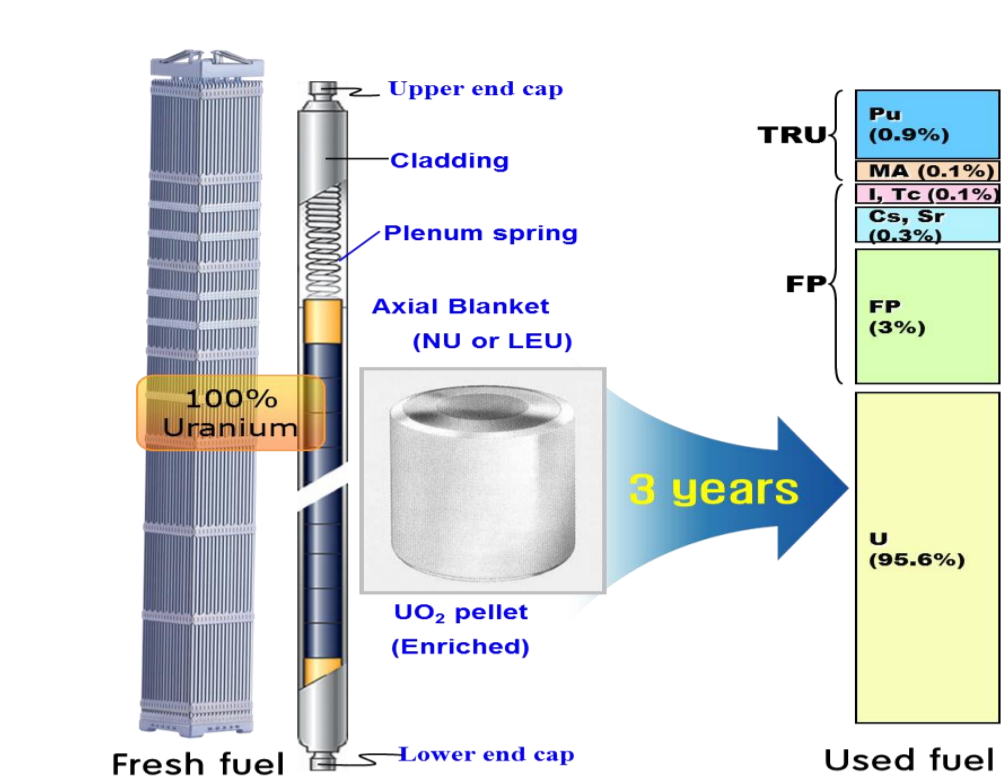
Study on the change in properties of uranium dioxide by co-doping of trivalent and tetravalent elements

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Introduction

Characterization of spent nuclear fuel



R.C. Ewing, Nature Mater. 14 (2015) 252-257

Component (fission product, burn-up)

Physical properties (structure, thermal conductivity)

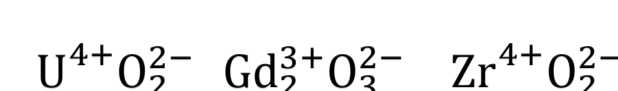
Chemical Properties (chemical state, oxidation, reactivity)

- How does the dopants affect the physical and chemical properties of uranium dioxide?
- The surface structures of Gd, Zr-doped UO₂ have been characterized by XRD and Raman spectroscopy
- The electrochemical behavior of Gd, Zr-doped UO₂ has been investigated using cyclic voltammetry

Experimental Details

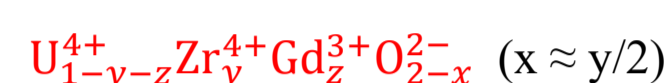
Preparation of pellet

Mixing of UO₂ and Gd₂O₃, ZrO₂ powder



Pressed into a disk pellet

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



Thickness: < 1 mm
Diameter: ~ 0.9 mm

XRD (X-Ray Diffraction)

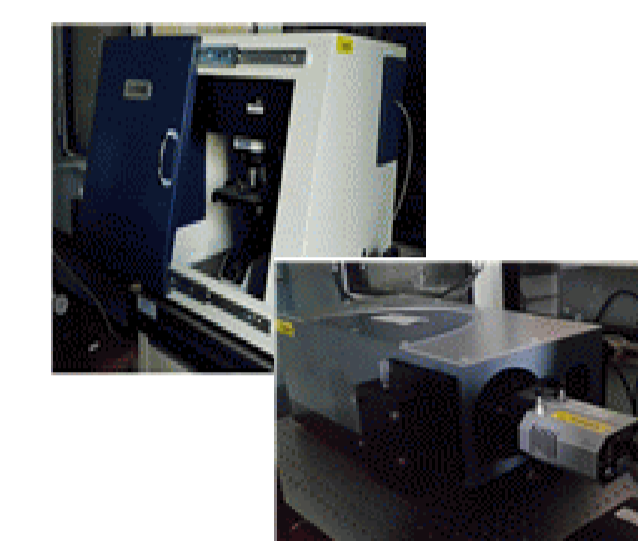


Bruker AXS D8 Advance X-ray Diffractometer using CuKα radiation at room temperature. The lattice parameters of the samples were calculated from refinement process using TOPAS program (Bruker Analytical X-Ray Systems) with the *Fm3m* space group.

SEM (Scanning Electron Microscopy)

Scanning electron microscopy (Jeol, USA) results, using 20 keV electron acceleration voltage with 10 mm of working distance, revealed morphological evolutions and grain features of freshly prepared pellet.

Raman spectroscopy

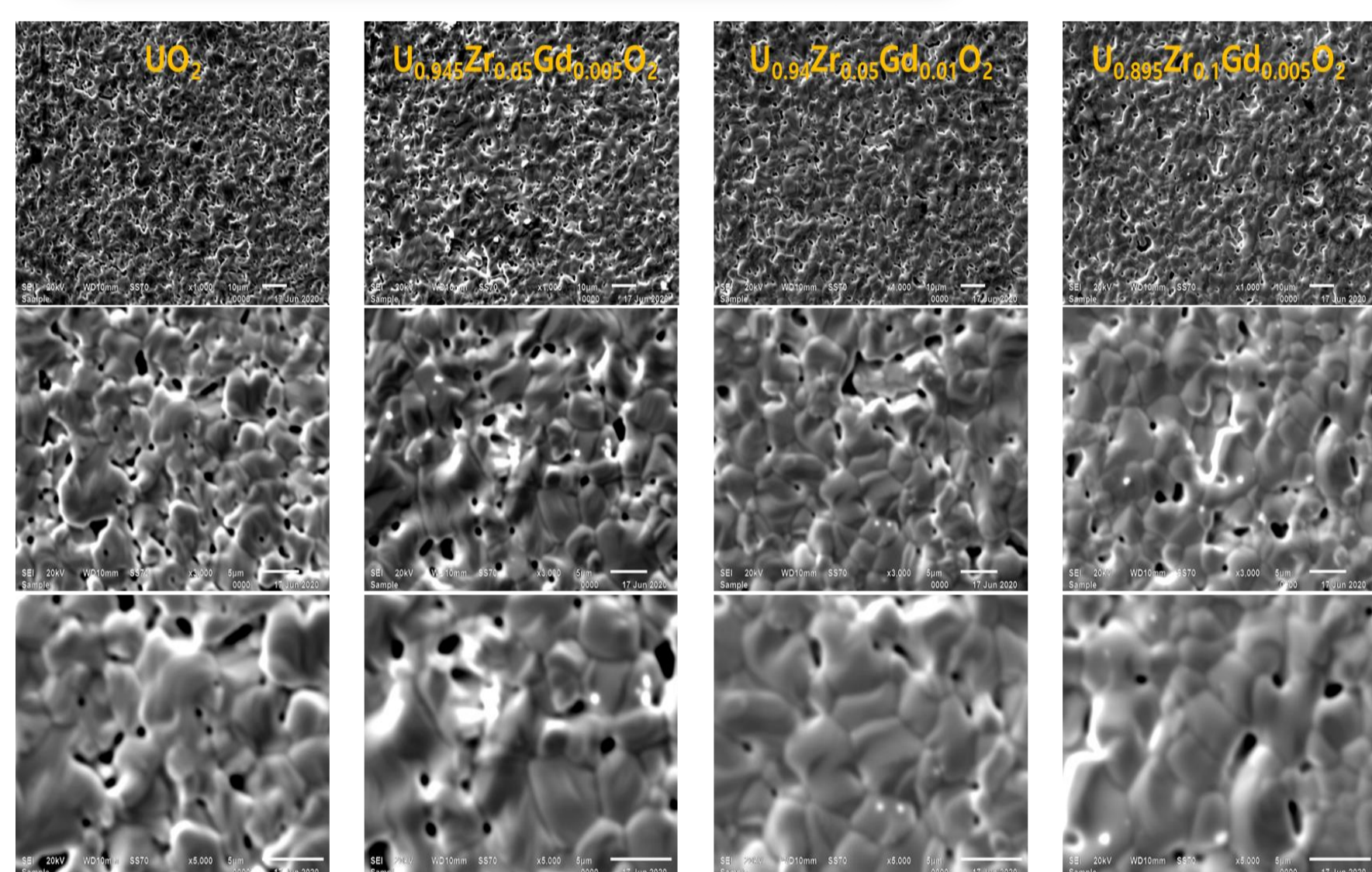


ANDOR Shamrock SR500i spectrometer with a 632.8 nm excitation of He-Ne laser. Raman spectra were measured at different locations on the surface of a pellet to confirm the homogeneity of the pellet and the reproducibility of the spectra

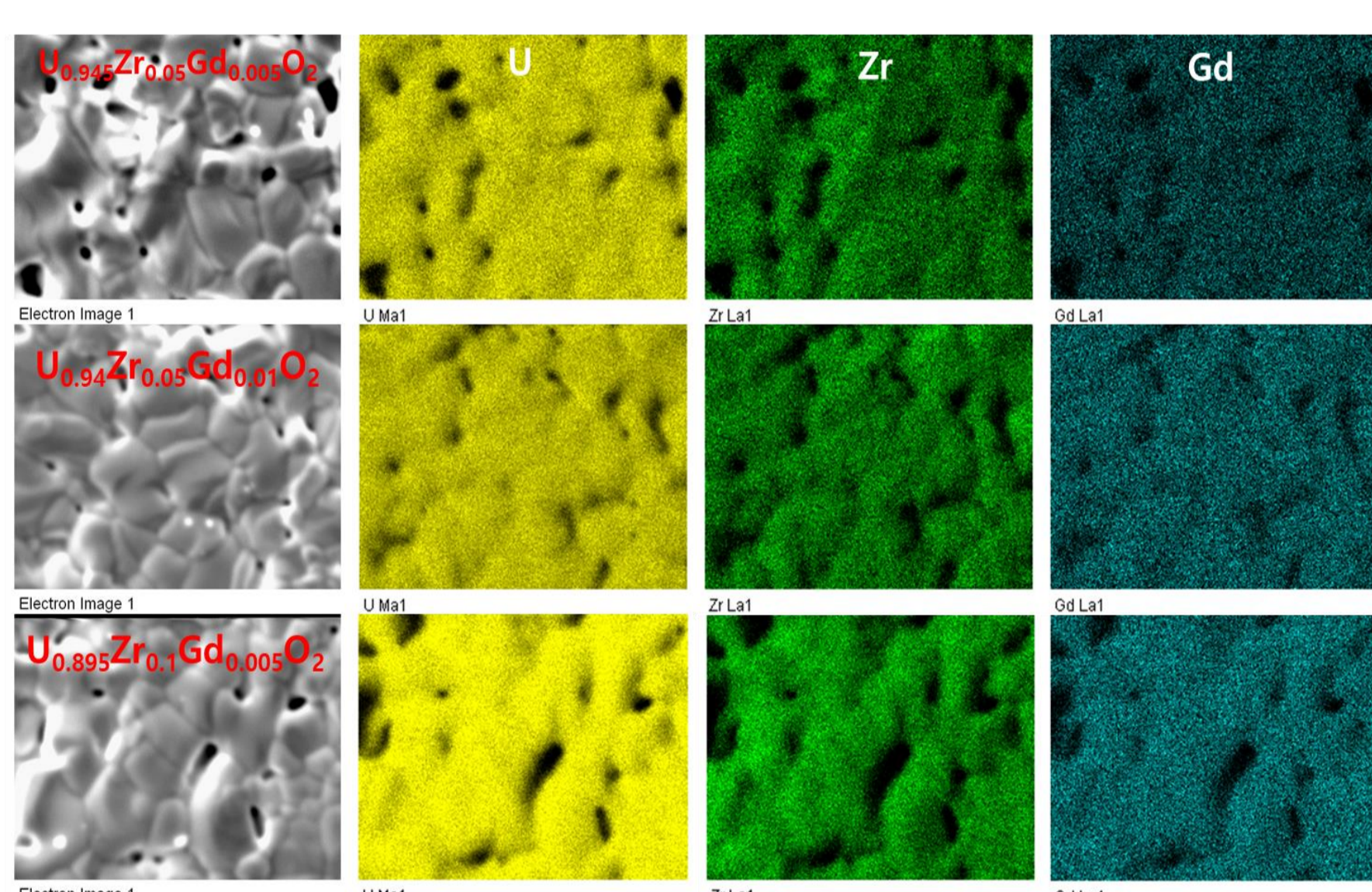
Electrochemical Experiment

Working electrodes were prepared by attaching pellets onto steel electrodes with using adhesive-conductive silver paste (DOTITE, Japan), and mounting pellets onto steel-working electrodes with using epoxy. Pt foil counter electrode (Aldrich, >99%) and commercial SCE reference electrodes (Saturated calomel electrode, Bruker) were used for setting up the three electrode system. All electrochemical experiments were carried out using CHI-600D potentiostat to control applied potentials and record current responses in 0.1 M NaClO₄(aq) with or without 0.01 M CO₃²⁻/HCO³⁻ at pH ~9.0.

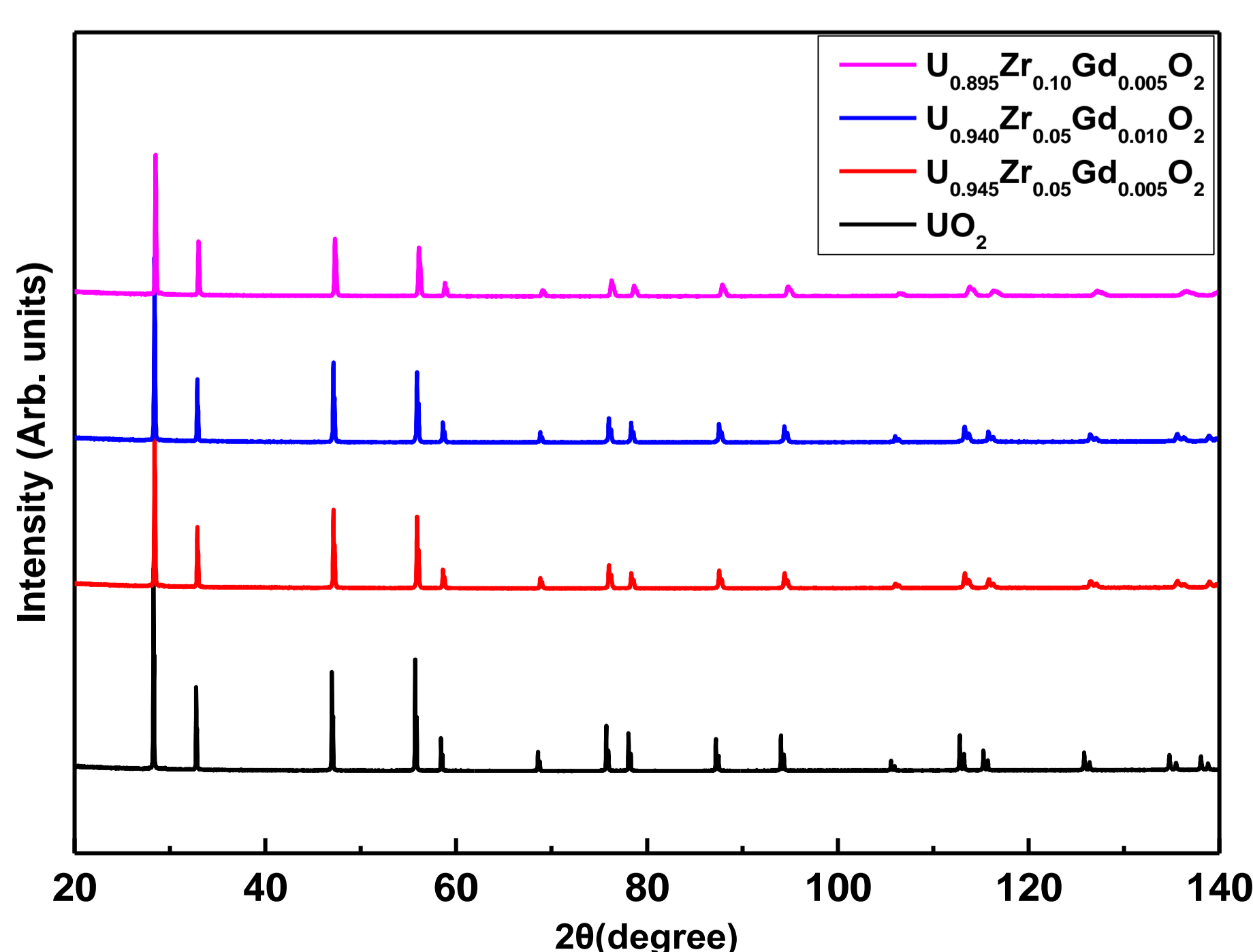
Results & Conclusions



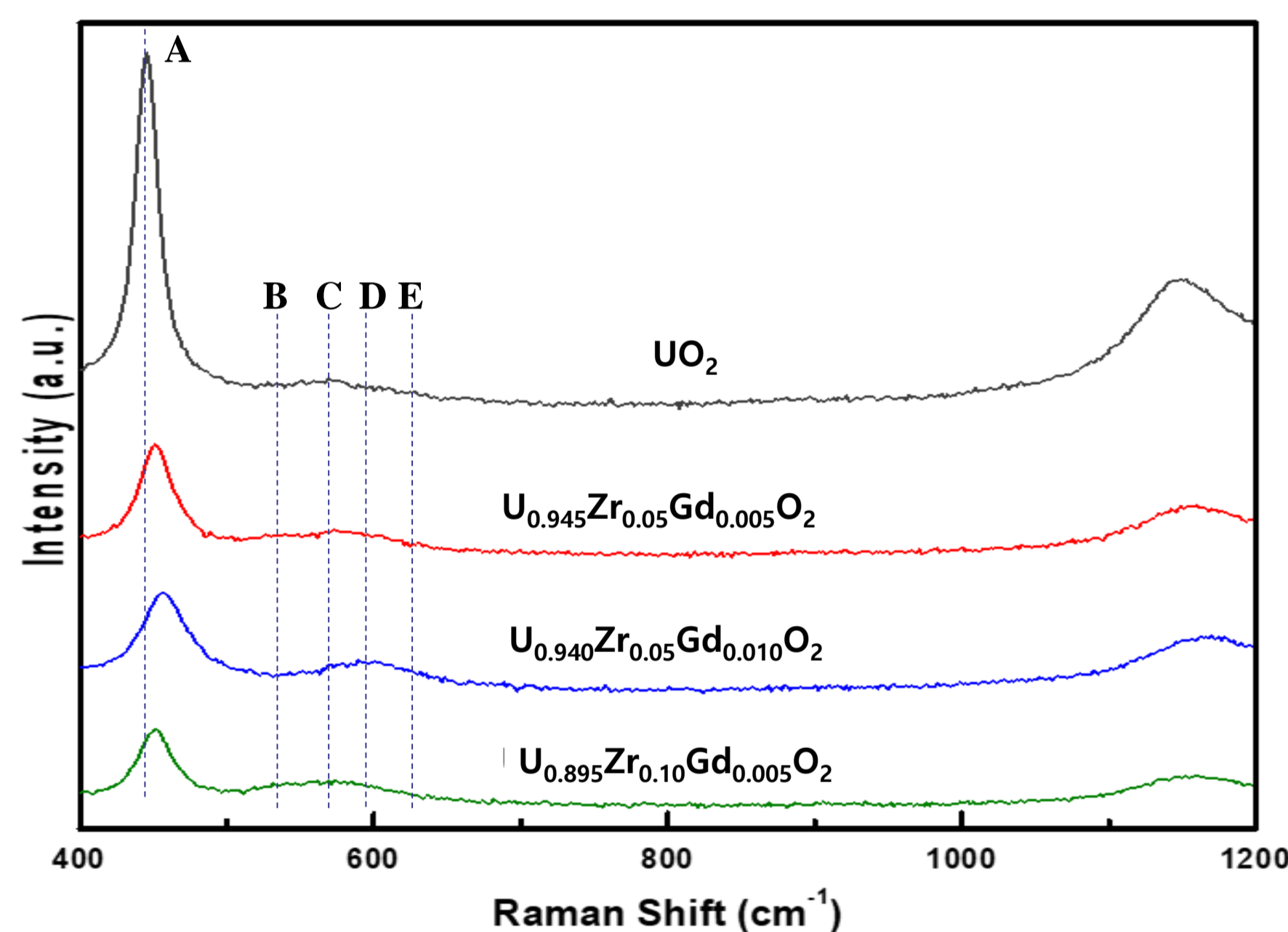
Comparing the domain structures on the surfaces of UO₂ and U_{1-y-z}Zr_yGd_zO₂



Comparing the element structures on the surfaces of U_{1-y-z}Zr_yGd_zO₂



XRD patterns of UO₂ (black) and U_{1-y-z}Zr_yGd_zO₂ pellets with y = 0.05, z = 0.005 (red), y = 0.05, z = 0.01 (blue), and y = 0.1, z = 0.005 (pink)



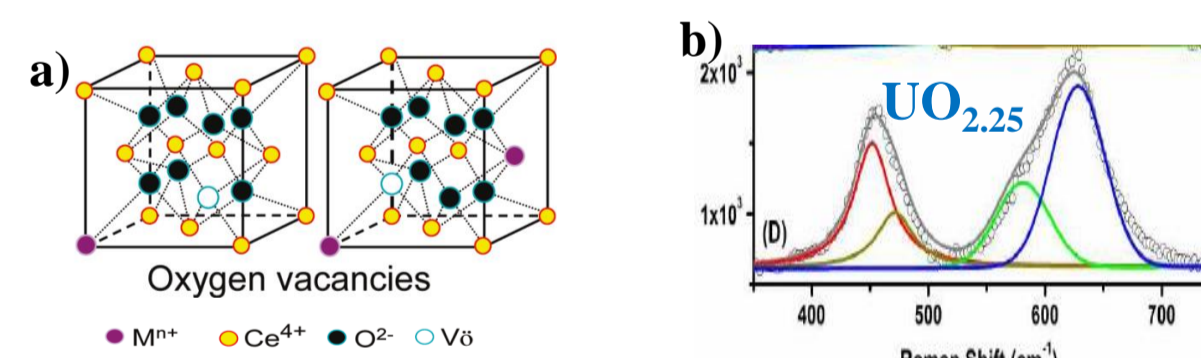
Raman spectra of UO₂ (black) and U_{1-y-z}Zr_yGd_zO₂ pellets with y = 0.05, z = 0.005 (red), y = 0.05, z = 0.01 (blue), and y = 0.1, z = 0.005 (pink)

A: T_{2g} at ~445 cm⁻¹

Fundamental U-O stretch at perfect fluorite structure

B: Peak at ~535 cm⁻¹

Local phonon mode associated with O_v-induced lattice distortion (creation of oxygen vacancies due to Gd³⁺)

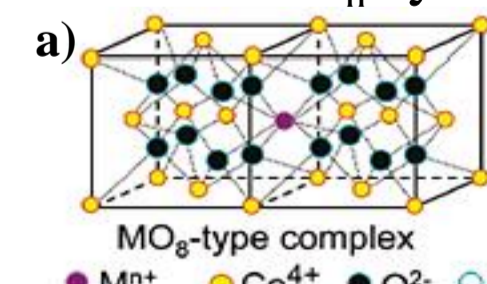


C: Peak at ~575 cm⁻¹

One L-O(Longitudinal-Optical) phonon band forbidden at perfect fluorite structure (~1150 cm⁻¹ is 2L-O phonons)

D: Peak at ~598 cm⁻¹

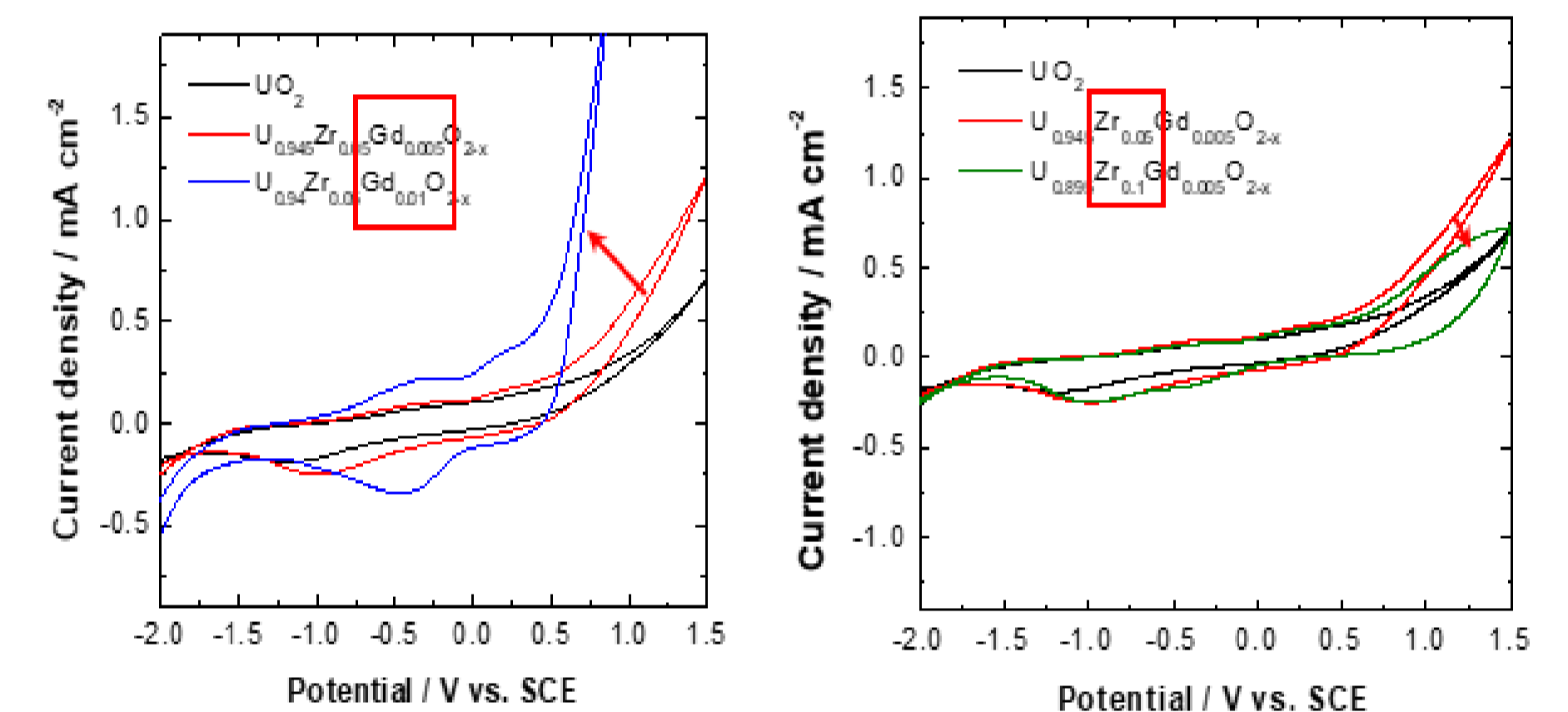
Attributed to the formation of a ZrO₈-type complex, in which Zr⁴⁺ is in an 8-fold coordination with O²⁻ with an O_h symmetry



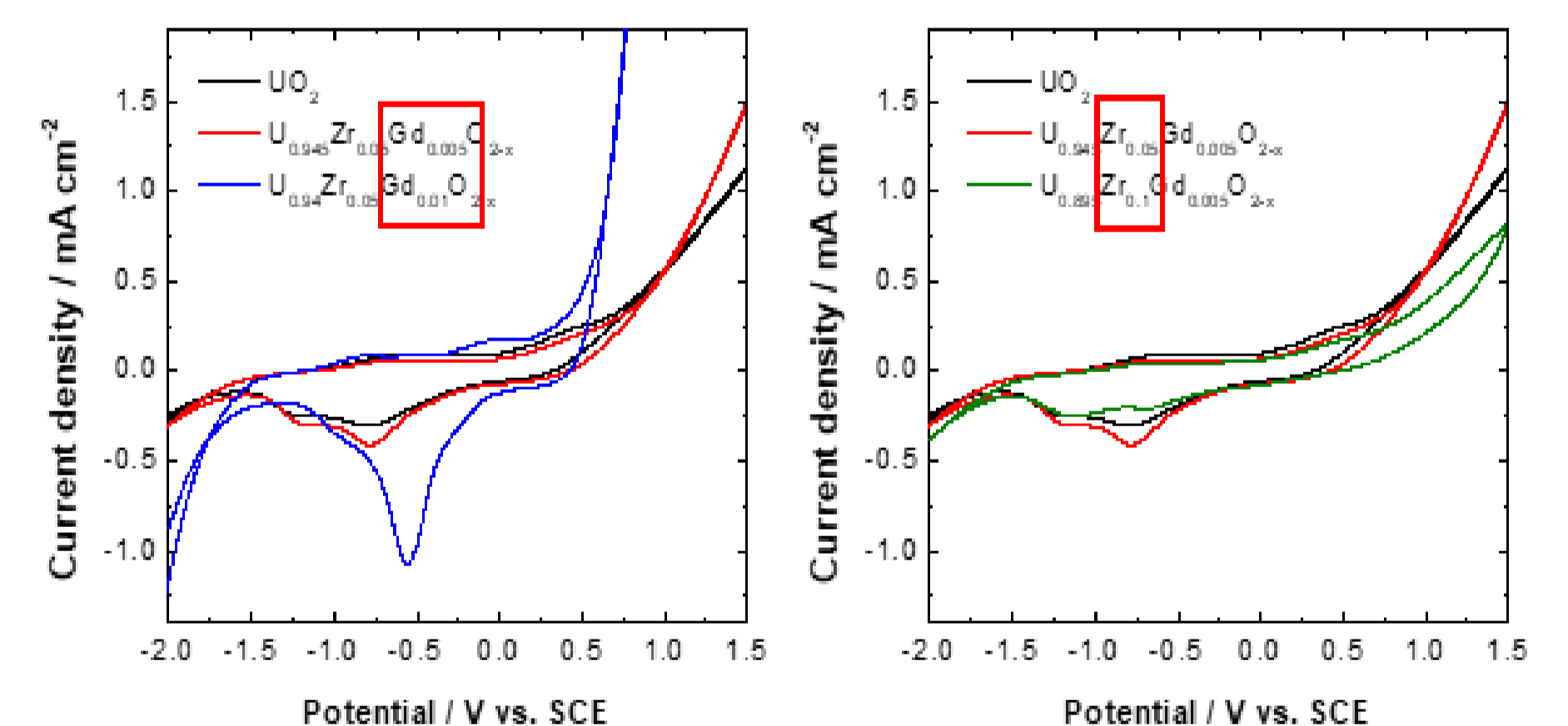
E: Peak at ~640 cm⁻¹

O sublattice distortions due to the O ion displacements required to accommodate the increasing amounts of excess O (Cubooctahedral constituting of the U₄O₉ phase)

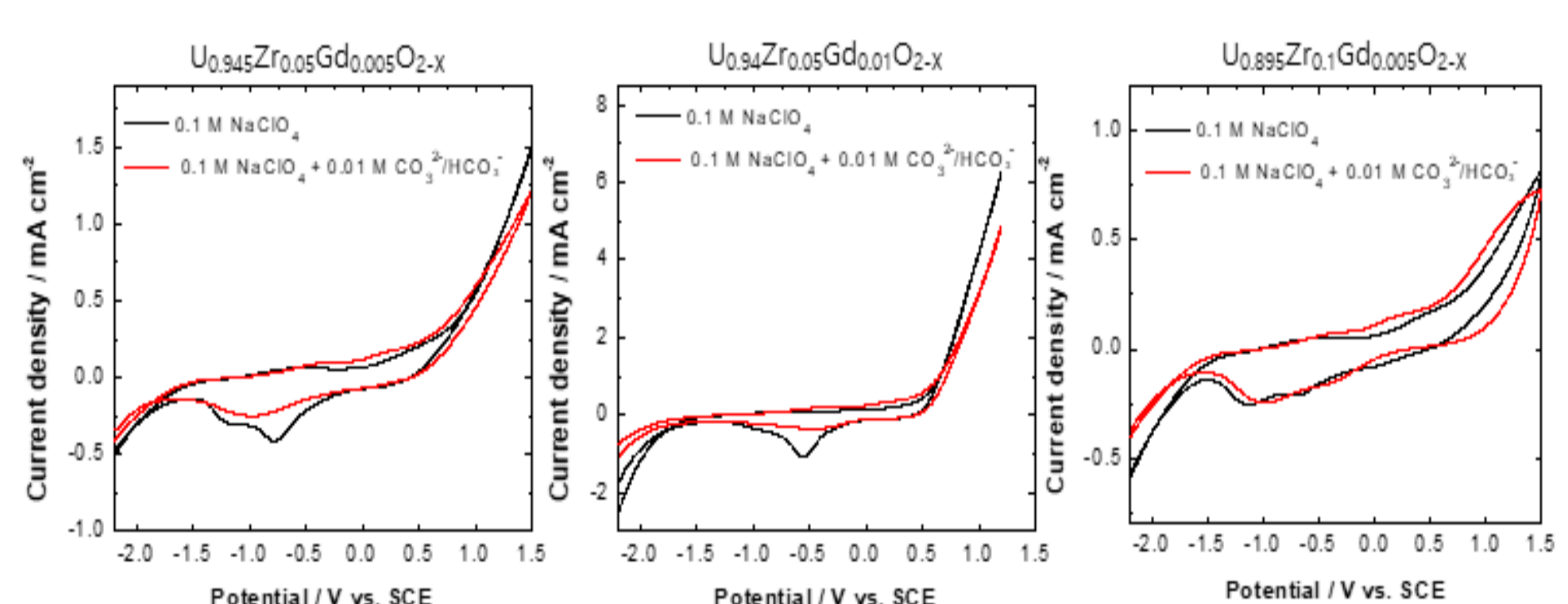
³¹L. Li et al., J. Phys. Chem. A 115 (2011) 7972-7977
³²H. He et al., Phys. Chem. Chem. Phys. 12 (2010) 8108-8117



Cyclic voltammograms of U_{1-y-z}Zr_yGd_zO₂ pellets (left : fixed Zr concentration, right : fixed Gd concentration) in 0.1 M NaClO₄(aq) + 0.01 M CO₃²⁻/HCO₃⁻. The pH of both solutions are adjusted to at 9.0. Scan rate is 0.05 V/sec.



Cyclic voltammograms of U_{1-y-z}Zr_yGd_zO₂ pellets (left : fixed Zr concentration, right : fixed Gd concentration) in 0.1 M NaClO₄(aq). The pH of both solutions are adjusted to at 9.0. Scan rate is 0.05 V/sec.



Compare of cyclic voltammograms of U_{1-y-z}Zr_yGd_zO₂ pellets with and without 0.01 M CO₃²⁻/HCO₃⁻ solution.

Conclusions

- A series of U_{1-y-z}Zr_yGd_zO₂ Samples were characterized by XRD and Raman spectroscopy to study the influence of Gd³⁺ and Zr⁴⁺ doping on the structure of U_{1-y-z}Zr_yGd_zO₂ solid solutions.
- XRD shows that the materials retain a fluorite lattice with increasing doping level.
- Raman spectroscopy shows that Gd³⁺ doping distorts the fluorite lattice structure, leading to the formation of oxygen vacancies (O_v) and, since both the oxidation state and ionic radius of Gd³⁺ differ from those of U⁴⁺.
- It was clearly shown that a ZrO₈-type complex forms in the fluorite UO₂ matrix via successive incorporation of the doped Zr.
- Oxidation of U_{1-y-z}Zr_yGd_zO₂ proceeded in two stages: (1) the oxidation of a thin surface layer to a mixed U⁴⁺/U⁵⁺ oxide; (2) the oxidation of this layer to U⁶⁺, which dissolved as U⁶⁺O₂(CO₃)₂²⁻ in the carbonate containing solution.
- Gd³⁺ doping affects the electrochemical oxidation of samples more than Zr⁴⁺ doping