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Dissolution of zirconium-cerium oxide solid solution in an aqueous system

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

The solid-solution aqueous-solution (SSAS) system often involves dissolution/precipitation and redox reactions simultaneously. Comprehensive understanding of the SSAS system requires a mechanistic insight into the dissolution mechanism of solid-solution based on reliable characterisation of solid phases. Given this background, this study investigates the dissolution behaviour of zirconium-cerium oxide solid solution ((Zr,Ce)O₂/(Ce,Zr)O₂), which contains a redox-active metal of Ce (Ce(III/IV)) and is of particular importance in nuclear industry. The solid phases of the solid-solution were comprehensively characterised by powder X-ray diffraction (PXRD) with the Rietveld analysis and X-ray absorption spectroscopy (XAS) with factor analysis, indicating that the solid-solution is primarily composed of tetragonal-(Zr,Ce)O₂ and cubic-(Ce,Zr)O₂. Water immersion of the solid-solution leads to the dissolution of the solid phase at the solid-liquid interface. The addition of a reductant to the system reduces Ce(IV) in the solid-solution to -(III) at the surface, promoting the dissolution of Ce from the solid-solution phase. The release of Ce from the solid-solution also enriches the Zr content in the remaining solid-solution phase at the surface to be more insoluble. This results in the formation of a protective layer at the solid surface, retarding further dissolution of the solid-solution phase.

1. Introduction

Oxide solid solution of tetravalent metals is one of the crucial materials in nuclear industry. For instance, the oxide solid solution of tetravalent actinides (An(IV)) is key components of mixed oxide (MOX) fuels¹ and spent nuclear fuels (SNFs).² As a result of irradiation of nuclear fuels, the oxide solid solution of uranium (U(IV)) and fission products (FPs) containing tetravalent metals (e.g. zirconium (Zr(IV)) or cerium (Ce(IV))) is formed in the fuels.³ The corrosion of structure/cladding materials composed of zirconium alloy (zircaloy) results in the formation of zirconium dioxide (ZrO₂),⁴ which potentially forms solid solutions with An and FPs.⁵

Amongst the oxide solid solution of tetravalent metals in nuclear industry, the ZrO₂-based solid solution with other metals is a versatile material particularly for the management and disposal of radioactive wastes (RAW). The solid solution of ZrO₂ and AnO₂ is considered to be a promising candidate as an inert matrix fuel for the transmutation of long-lived radionuclides.⁶ The remarkably high stability, durability, and resistivity of ZrO₂ (particularly in the cubic system) makes itself an ideal host material for the long-term secure storage of RAW, forming the ZrO₂-based solid solution with An and FPs in the wastes.^{5,7} In addition to the management/disposal of RAW,

the solid solution of ZrO₂ and AnO₂ can be also formed as a component of "nuclear fuel debris", which is also treated as RAW in the end, after the severe accidents of nuclear reactors.^{8,9} Hence, the oxide solid solution of Zr(IV) and An(IV) is an important material for the management and disposal of RAW in many contexts.

RAW is stored and disposed of in the aqueous environment,¹⁰ under which the migration of radionuclides potentially leaching out of the wastes is controlled by the dissolution and (re-)precipitation. This means that the leaching behaviour of the waste material is a matter of critical concern for the safety assessment of the management and disposal of RAW. For this reason, the solubility of nuclear-related elements/compounds have been extensively investigated mainly in terms of thermodynamics, including Zr/ZrO₂,¹¹ An/AnO₂,¹² and solid solution of AnO₂.¹³ Additionally, the solubility of (Zr,U)O₂ solid solution has been actively investigated in the last decade for understanding the potential migration behaviour of radionuclides in the nuclear fuel debris that still remains in the damaged nuclear reactors at the Fukushima Dai-ichi Nuclear Power Station.¹⁴⁻¹⁸ These precedent studies contribute to describing the dissolution/precipitation behaviour of a wide range of elements/compounds at the equilibrium. They provide, however, less mechanistic insight into the dissolution and precipitation phenomena. The reliable assessment for the management and disposal of RAW requires comprehensive understanding of the dissolution and precipitation phenomena based on both thermodynamics and reaction mechanism. This motivates us to perform the present study aiming at gaining both mechanistic and thermodynamic insights into the dissolution/precipitation of oxide solid solution containing redox-active metals.

As mentioned above, the oxide solid solution of Zr(IV) and An(IV) is a material of significant concern for the management and disposal of RAW. However, the radioactivity of An often renders practical work with An-containing materials difficult, where non-radioactive

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† Supplementary Information available: Measurement data (PXRD, XANES, and SEM) and experimental details not provided in the main text. See DOI: 10.1039/x0xx00000x

surrogates are often employed as an alternative. As a non-radioactive surrogate of An(IV), Ce(IV) is known to be a competent analogue,^{19–22} which is used also for simulating the oxide solid solution systems^{23, 24} including the ZrO₂-based solid solution containing An(IV).^{25, 26} Given this background, this study investigates the oxide solid solution of Zr(IV) and Ce(IV) (referred to as "Zr/Ce oxide s.s." hereafter) to simulate the oxide solid solution system containing Zr(IV) and An(IV). In this study, a series of "Zr/Ce oxide s.s." with different Zr/Ce ratios were prepared and immersed in aqueous solutions with different pH values. The solid samples before and after the immersion were comprehensively characterised by powder X-ray diffraction (PXRD) and X-ray absorption spectroscopy (XAS). The mechanisms of dissolution and precipitation of "Zr/Ce oxide s.s." are discussed based on the results of structure characterization together with those of solubility measurements.

In oxide materials or under aqueous conditions, Zr exists exclusively as Zr(IV). On the other hand, Ce is redox-active and can exist as Ce(III) and -IV). Hence, the dissolution/precipitation of "Zr/Ce oxide s.s." potentially involves the redox reaction of Ce(III/IV), which complicates the understanding of the dissolution and precipitation phenomena as a whole. The combination of dissolution/precipitation and redox reactions are of importance not only for the present study relevant to nuclear industry, but also to geology in general. In geology, dissolution/precipitation and redox reactions have been investigated often in terms of the solid-solution aqueous-solution (SSAS) systems.²⁷ The study on SSAS systems dealing with both dissolution/precipitation and redox reactions simultaneously is, however, rather scarce even in geology as far as we know. Given this background, this study attempts to describe the dissolution/precipitation of "Zr/Ce oxide s.s." by taking redox reactions into account, which is also relevant to the oxide solid solution of Zr and An that are also redox-active.

2. Experimental

2.1 Materials and analytical apparatus

Zirconyl dinitrate dihydrate (Zr(NO₃)₂·2H₂O, 97.0%) and diammonium cerium(IV) hexanitrate (Ce(NH₄)₂(NO₃)₆, 95.0%) were used to prepare the stock solutions of Zr(IV) and Ce(IV), respectively ([M(IV)] = 0.5 mol/L). Tin dichloride (Sn(II)Cl₂, 99.9 %) was employed as a reductant. All the chemicals were purchased from FUJIFILM Wako Chemicals and used as received.

A combined glass electrode (9615-10D, Horiba Ltd.) and a combined Pt electrode (9300-10D, Horiba Ltd.) equipped with a Ag/AgCl reference were used for the measurements of hydrogen ion concentrations (pH_c) and redox potentials, respectively. The electrodes were filled with 3.6 mol/L NaCl and 0.4 mol/L NaClO₄ to prevent the precipitation containing potassium (K) at the liquid junctions. The electrodes were calibrated against standard HNO₃ and NaOH solutions (pH_c = 1, 2, 3, 11, 12, and 13; >99.0%, FUJIFILM Wako Chemicals) by adjusting the ionic strength (*I*) at 0.5 mol/L with NaNO₃. Based on the measured pH_c values, experimental pH values (pH_{exp}) were calculated by using the equation "pH_c = A × pH_{exp} + B", where A and B are correction factors that have been experimentally determined to be 1.04 and −0.20, respectively.²⁸ The measured redox potential values were converted into Eh (the redox potential against the standard hydrogen electrode) by the addition of +208 mV on the values. The apparent electron activity (pe = −log *a*_{e−}) was calculated with the equation "Eh = −(RT/F) ln *a*_{e−}", according to the relation pe = 16.9 Eh (V) at 25 °C. The errors in the pH_c and Eh values

were estimated to be ±0.05 and ±20 mV (about 0.3 pe units), respectively.

2.2 Preparation of "Zr/Ce oxide s.s."

The oxide solid solution of Zr(IV) and Ce(IV) (i.e. "Zr/Ce oxide s.s.") was synthesised via a polymeric steric entrapment method.^{29, 30} The stock solutions of Zr(IV) and Ce(IV) were mixed with different Zr/Ce molar ratios (10/0, 9/1, 7/3, 5/5, 3/7, 1/9, and 0/10) with a total metal concentration ([Zr] + [Ce]) of 0.5 mol/L, and the mixed solution was added to 0.5 mol/L polyvinyl alcohol (PVA) solution (PVA 3500, 78% hydrolyzed, FUJIFILM Wako Chemicals). The resulting solutions were mixed for an hour with a magnetic stirrer and evaporated at 200 °C for two hours. The obtained solid products were heated for 2–6 hours at 1,000 °C in a muffle furnace (FO-100, Yamato Scientific Co.) and then cooled in the furnace.

For immersion experiments, the prepared "Zr/Ce oxide s.s." powder was soaked in 0.5 mol/L NaClO₄ for 36 days at 25 °C under an atmospheric pressure (ca. 1 atm). The samples were manually shaken on occasion for a few minutes during the experiments. For the samples with Zr/Ce molar ratios of 7/3 and 3/7, 10 ml of 0.01 mol/L SnCl₂ was added into the sample solutions in an inert glove box filled with Ar gas (>99.998%-purity) in order to investigate the possible effects of the reductant on the dissolution/precipitation behaviour of "Zr/Ce oxide s.s.". In the same manner, immersion experiments with CeO₂ and CeO₂ nanopowder were also performed with and without SnCl₂ for comparison. 500 mg of the sample powder was soaked in 50 mL of the NaClO₄ solution for solid phase characterization, whilst 10 mg of the sample powder was soaked in 10 mL of the NaClO₄ solution for solubility measurements. Assuming pure CeO₂, 10 mg of CeO₂ powder contains 0.058 mmol of Ce, whilst 10 ml of 0.01 mol/L SnCl₂ equals to 0.1 mmol of Sn(II). Hence, the amount of the reductant added to the samples was sufficient to reduce to all the Ce in the samples.

2.3 Solid phase characterization

In order to characterise the solid phases of the synthesised "Zr/Ce oxide s.s." samples before and after immersion, PXRD patterns were collected on a MiniFlex diffractometer (Rigaku) with Cu-Kα radiation (λ = 0.154 nm) in the diffraction range (2θ) from 20 to 90° at a scan rate of 5°/min with a step of 0.01°. Prior to the measurement, the samples were dried at 25 °C in a vacuum desiccator. The collected diffraction patterns were treated, fitted, and refined with the Rietveld method using the Rigaku SmartLab Studio II software.³¹ For Rietveld refinement, cubic CeO₂ (CeO₂(c)) (ICSD No. 28753, *Fm* $\bar{3}$ *m*) and tetragonal ZrO₂ (ZrO₂(t)) (ICSD No. 23928, *P4*₂/*nmcS*) were initially assigned, and variables (background, lattice parameters, scale factor, and peak profiles) were all refined. The purchased compounds of ZrO₂ (FUJIFILM Wako Chemicals), CeO₂ (FUJIFILM Wako Chemicals), and CeO₂ nanopowder (Sigma-Aldrich/Merck) were also characterised by PXRD to be monoclinic ZrO₂ (ZrO₂(m)) (ICSD No. 18190, *P2*₁/*c*) and CeO₂(c). The crystalline size of CeO₂ and CeO₂ nanopowder was estimated to be 84 and 22 nm (assuming sphere particles), respectively, based on the PXRD profiles.

The "Zr/Ce oxide s.s." samples before and after immersion were also characterised by XAS including the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions. XAS measurements were performed at Zr K-edge (17.998 keV) and Ce K-edge (40.447 keV) on the beamline BL14B1, SPring-8 (Hyogo, Japan) using a Si(311) double-crystal monochromator. Monochromatic X-ray radiation (~1010 photons/s

at Zr and Ce K-edges) was focused on a spot of $\sim 3 \times 1 \text{ mm}^2$ (horizontal $\times$ vertical) at the sample position. Higher order harmonics in the incident X-rays were suppressed by two Rh-coated mirrors. X-ray absorption spectra were recorded in a transmission mode using ionization chambers filled with Ar/N₂ mixture (Ar/N₂ = 1/1) at ambient temperature and pressure. The spectra for ZrO₂(m), CeO₂(c), and Ce₂(SO₄)₃ were also collected as references. Data treatment and analysis for the collected X-ray absorption spectra were performed according to a standard procedure using the Demeter software package (version 0.9.18)³² and WinXAS (version 3.2).³³ A suite of factor analysis (FA) including target testing (TT) and iterative target transformation (ITT) was performed both on the XANES and EXAFS spectra of Zr K- and Ce K-edges using the program code iterative target-transformation factor analysis (ITFA) developed by Rossberg.³⁴ The solid phase samples for PXRD and XAS are summarised in **Tables 1–3**. Hereafter, the synthesised "Zr/Ce oxide s.s." samples were referred to with the IDs in **Tables 1–3**.

(Table data are provided on the final page.)

Table 1 Summary of "Zr/Ce oxide s.s." samples with different Zr/Ce molar ratios

Table 2 Summary of "Zr/Ce oxide s.s." samples (70 mol%-Zr: ZC73)) for immersion experiments

Table 3 Summary of "Zr/Ce oxide s.s." samples (30 mol%-Zr: ZC73)) for immersion experiments

2.4 Solubility measurement

Solubility measurements for the synthesised "Zr/Ce oxide s.s." samples without a reductant (SnCl₂) were performed at 25 °C under an atmospheric pressure (ca. 1 atm), whilst the measurements for the samples with the reductant were conducted in an inert glove box filled with Ar gas (>99.998%-purity). Prior to sample collection, pH_c and Eh of the sample solutions were measured. 0.5 mL of supernatant were collected from the sample solutions and filtered with an ultrafiltration membrane (3 kDa; Millipore) at 25 °C. 0.3 mL of the filtrate was then acidified with 0.1 mol/L HNO₃, and Zr and Ce concentrations in the samples were measured by inductively coupled plasma mass spectrometry (ICP-MS; ELANDRC II, PerkinElmer). The detection limit of the instrument was $\sim 10^{-9}$ mol/L for Zr and Ce with the standard error of $\sim 10\%$.

3. Results

3.1 Powder X-ray diffraction

3.1.1 PXRD characterization before immersion

Shown in **Fig. 1** are the PXRD patterns for a series of the synthesised "Zr/Ce oxide s.s." samples with different Zr/Ce molar ratios from 0/10 to 10/0, together with the pattern of a simple mixture of ZrO₂ and CeO₂ powder (Zr/Ce = 5/5) without heat treatment. The PXRD patterns for ZC010 and ZC100 (= pure CeO₂ and ZrO₂ powder) were confirmed to be CeO₂(c) and ZrO₂(m), respectively. The diffraction peaks of CeO₂(c) and ZrO₂(m) phases were clearly separated in the simple mixture of ZrO₂ and CeO₂ powder (the bottom data in **Fig. 1**), indicating that these two phases are sufficiently distinguishable by

PXRD. The sample ZC19 shows the PXRD pattern that is comparable to that of CeO₂(c). This is in consistent with the reported Zr-Ce-O systems^{35–41} where 10 mol%-Zr is close to the border between a complete solid solution of (Ce,Zr)O₂(c) with possible phase separation into ZrO₂(m) or ZrO₂(t)-based solid solution (i.e. (Zr,Ce)O₂(t)) at 1,000 °C. When the Zr ratio increased to 30 mol% (= ZC37), ZrO₂(t) emerged and grew with increasing the Zr ratio, which is also consistent with the reported phase diagram.⁴⁰ It has been reported that heating the hydrous coprecipitate obtained from a mixture of aqueous Ce(NO₃)₃ and ZrCl₄ solutions with NH₄OH at 1,000 °C results in the formation of cubic and monoclinic phases,⁴⁰ whilst our preparation (drying the mixture of ZrO(NO₃)₂, Ce(NH₄)₂(NO₃)₆, and PVA solutions and heating at 1,000 °C) ended in the formation of tetragonal + cubic phases. This clearly suggests that starting materials and synthetic conditions affect the final products of solid phases. ZrO₂(t) became dominant at ZC73 (70 mol%-Zr) and the peaks corresponding to ZrO₂(m) emerged at ZC91 (90 mol%-Zr), as expected from the phase diagram. The PXRD patterns for the series of the "Zr/Ce oxide s.s." samples were unchanged when heating duration varied from 2 to 6 hours at 1,000 °C. Given these results, ZC73 and -37 samples prepared by heating at 1,000 °C for 4 hours were selected for the following immersion experiments to cover major tetragonal and cubic phases as bulk.

3.1.2 PXRD characterization after immersion

The solid phases of ZC73 and -37 after immersion in 0.5 mol/L NaClO₄ were characterized by PXRD, the results of which are given in **Fig. 2**. When the reductant (SnCl₂) was not added in the immersing solution, the PXRD profile was unchanged before and after immersion both for ZC73 and -37 samples. This indicates that (at least) the bulk structure of "Zr/Ce oxide s.s." is insusceptible to aqueous immersion without the reductant. In contrast, when the reductant was added in the immersing solution, the peaks corresponding to CeO₂(c) emerged for ZC73 with pH < 3, whilst the peaks associated with ZrO₂(t) became more obvious for ZC37 with pH > 3. These changes in PXRD profiles were further analysed with Rietveld refinement.

For further analysis, the lattice parameters of CeO₂(c) and ZrO₂(t) phases in "Zr/Ce oxide s.s." were estimated by the Rietveld refinement, the results of which are summarised in **Fig. 3** and **Table S1** in Electronic Supporting Information (ESI). It is obvious from **Figs. 1 and 2** that the major phases of ZC73 and -37 before immersion are ZrO₂(t) and CeO₂(c), respectively, whilst the minor phases are the opposite (i.e. CeO₂(c) and ZrO₂(t), respectively).

For ZC73 before immersion, the lattice parameters of ZrO₂(t) (the major phase) were estimated to be $a = b = 3.65 \text{ \AA}$ and $c = 5.25 \text{ \AA}$, which are comparable to those of 3.64 and 5.27 Å for reference ZrO₂(t) (ICSD No. 23928). In contrast, the lattice parameter of CeO₂(c) (the minor phase) was $a = b = c = 5.35 \text{ \AA}$, which is significantly shorter than 5.41 Å for reference CeO₂(c) (ICSD No. 28753), indicating the formation of (Ce,Zr)O₂(c) solid solution as the minor phase. Based on the Vegard law with $a = 5.41 \text{ \AA}$ for CeO₂(c) and 5.10 Å for ZrO₂(c) (ICSD No. 53998), approximately 20 mol% Zr is estimated to be dissolved in the CeO₂(c) matrix. When the "Zr/Ce oxide s.s." ZC73 was immersed in 0.5 mol/L NaClO₄, the lattice parameters of the major ZrO₂(t) phase were found to remain unchanged regardless of the solution pH_c and the presence/absence of a reductant (SnCl₂) (**Fig. 3-(a)**), whilst the minor CeO₂(c) phase (i.e. (Ce,Zr)O₂(c)) expanded under the acidic condition with the reductant (Samples 6–9 in **Fig. 3-(b)**).

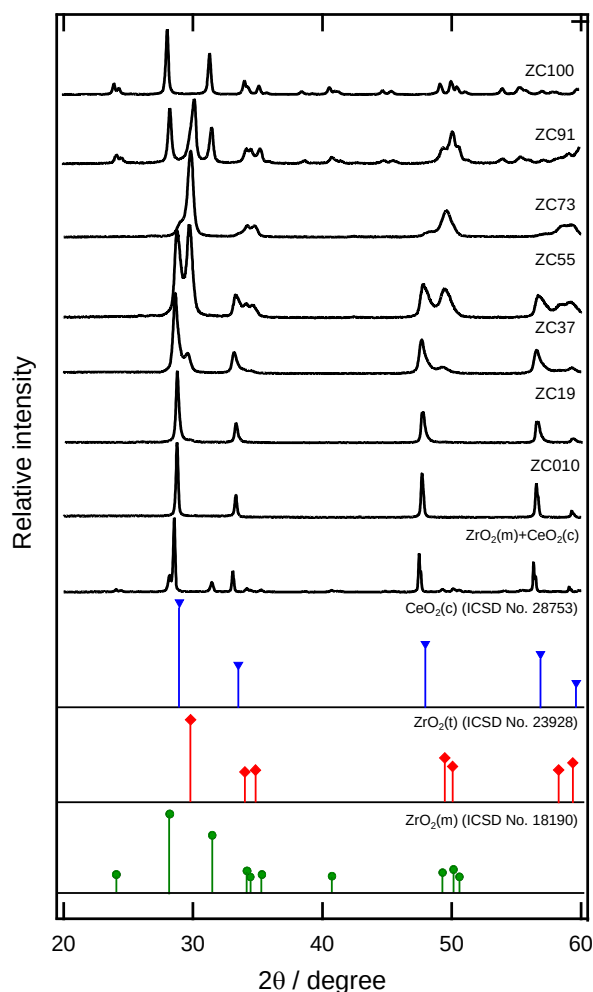


Figure 1. PXRD profiles of solid phases obtained by heating the mixture of ZrO_2 and CeO_2 powder with different Zr/Ce ratios at 1,000 °C for four hours together with a simple mixture of ZrO_2 and CeO_2 powder (Zr/Ce = 5/5) without heating. Sample IDs (ZC100-010) correspond to the IDs in Table 1.

The trend in phase transformation became the opposite for ZC37. The lattice parameter for the major $\text{CeO}_2(\text{c})$ phase was determined to be 5.38 Å. This is slightly shorter than 5.41 Å for reference $\text{CeO}_2(\text{c})$, indicating possible formation of $(\text{Ce,Zr})\text{O}_2(\text{c})$ solid solution containing 10 mol%-Zr based on the Vegard law. This $\text{CeO}_2(\text{c})$ -based major phase appeared to remain unchanged even after immersion (Fig. 3-(d)). The lattice parameters for the minor $\text{ZrO}_2(\text{t})$ phase before immersion were found to be 3.69 Å for a and b , and 5.27 Å for c . Slight deviation of these values from the reference values ($a = b = 3.64$ Å and $c = 5.27$ Å for $\text{ZrO}_2(\text{t})$) suggests possible formation of $(\text{Zr,Ce})\text{O}_2(\text{t})$ solid solution. After immersion without the reductant, the lattice parameters stayed comparable to those before immersion (Samples 1, 2, and 4 in Fig. 3-(c)). However, the phase changed significantly when it was immersed with the reductant (Samples 6-12 in Fig. 3-(c)). This indicates that the minor $\text{ZrO}_2(\text{t})$ -based phase (i.e. $(\text{Zr,Ce})\text{O}_2(\text{t})$) is affected by the immersion with the reductant.

3.2 X-ray absorption spectroscopy

3.2.1 XANES

XANES is sensitive to the local structure and electronic state of absorbing atoms, providing information about the coordination

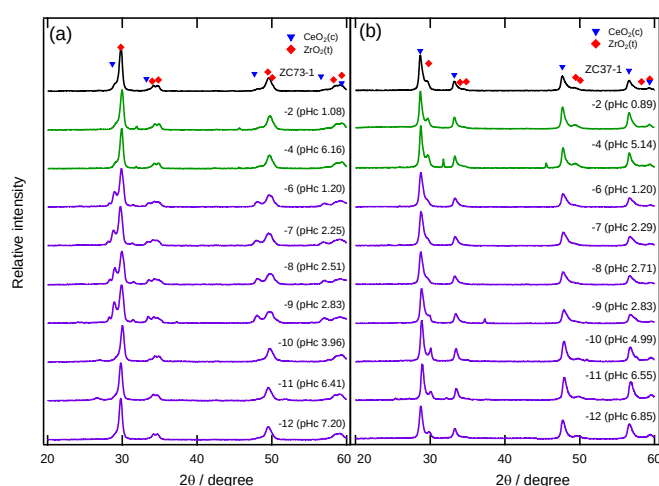


Figure 2. PXRD profiles of solid phases of the "Zr/Ce oxide s.s." samples after immersion in 0.5 mol/L NaClO_4 with different solution conditions: (a) Zr/Ce molar ratio = 7/3 (ZC73), and (b) 3/7 (ZC37). Sample IDs (ZC73/37-XY) correspond to the IDs in Tables 2 and 3. Black lines; before immersion, green lines; immersion without SnCl_2 (reductant), purple lines; immersion with SnCl_2 . Additional unassigned peaks are those of $\text{NaClO}_4(\text{o})$ (COD No. 1010214) originating from the immersing solution.

geometry ($\approx$ speciation) and oxidation states of target elements.⁴² In this study, series of the collected XANES spectra were analysed by factor analysis (FA) to extract principal spectral factors that compose the series of the analysed spectra.⁴³ Fig. S1 in ESI shows the absorption edge of Ce K-edge XANES spectra for Ce(IV) reference compounds, and the XANES spectra for a series of "ZC73" samples at Zr- and Ce K-edges are shown in Figs. S2-(a) and S3-(a) in ESI. The factor indicator function (IND), a powerful empirical function to estimate the proper number of principal factors,⁴⁴ indicated that the series of the spectra can be composed of two or three factors both for the Zr- and Ce K-edge XANES spectra (Fig. S4 in ESI). The reproduction of the series of the spectra with two principal factors showed no significant difference with the reproduction with three principal factors, suggesting that two principal factors are sufficient

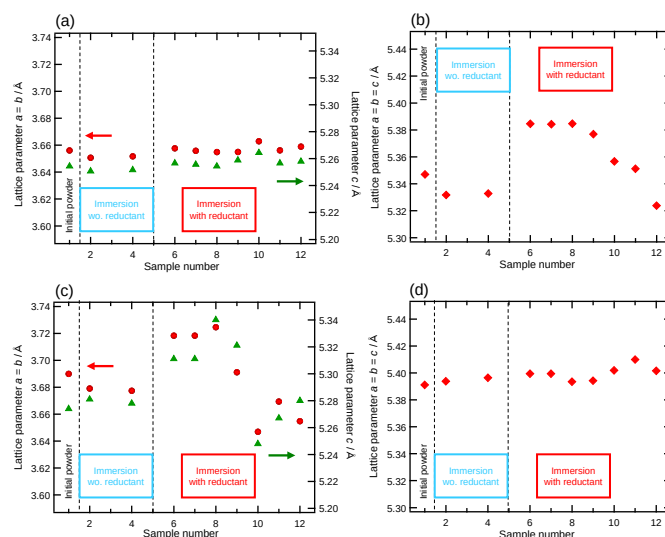


Figure 3. Variation in lattice parameters of $\text{ZrO}_2(\text{t})$ and $\text{CeO}_2(\text{c})$ phases before and after immersion. (a) $\text{ZrO}_2(\text{t})$ and (b) $\text{CeO}_2(\text{c})$ in ZC73, (c) $\text{ZrO}_2(\text{t})$ and (d) $\text{CeO}_2(\text{c})$ in ZC37. The values were obtained by the Rietveld refinement. Sample numbers correspond to the numbers of Sample ID in Tables 2 and 3.

to reproduce the series of the XANES spectra both at Zr- and Ce K-edges. Given this result, the series of the XANES spectra were further analysed by FA with two principal factors. The XANES spectra of the extracted two principal factors are given in **Figs. S2-(b)** and **S3-(b)** in ESI.

In terms of oxidation states, Zr exists exclusively as tetravalent (Zr(IV)) in oxides, whilst Ce can be present in oxides as tri- and/or tetravalent (Ce(III) and/or Ce(IV)). At Zr K-edge, one of the extracted factors (Factor 2 in **Fig. S2-(b)**, ESI) corresponds to the spectrum of $\text{ZrO}_2(\text{t})$, and the other factor (Factor 1 in **Fig. S2-(b)**, ESI) exhibits the spectral shape comparable to that of $\text{ZrO}_2(\text{t})$ (= Factor 2). This suggests that the series of "ZC73" samples presumably contains $\text{ZrO}_2(\text{t})$ and another phase that is structurally similar to $\text{ZrO}_2(\text{t})$. At Ce K-edge, $\text{CeO}_2(\text{c})$ is extracted as one of the two principal factors (Factor 1 in **Fig. S3-(b)**, ESI). The spectrum of the other factor (Factor 2 in **Fig. S3-(b)**, ESI) is well comparable to that of $\text{CeO}_2(\text{c})$, but it slightly shifts to higher energy. As the absorption edge of Ce(III) compounds is lower in energy than that of Ce(IV) ones (Section S1 in ESI), the extracted XANES spectra in **Fig. S3-(b)** in ESI indicate that Ce in "ZC73" samples is mainly in the tetravalent state (i.e. Ce(IV)), and its structure is $\text{CeO}_2(\text{c})$ and its comparable form.

Shown in **Figs. S5-(a)** and **S6-(a)** in ESI are the XANES spectra at Zr- and Ce K-edges, respectively, for a series of "ZC37" samples. As is the case for "ZC73", the series of the spectra can be reproduced by FA reasonably with two principal factors (**Fig. S7** in ESI), and the spectra of $\text{ZrO}_2(\text{t})$ and $\text{CeO}_2(\text{c})$ were extracted as one of the two principal factors at Zr- and Ce K-edges, respectively (**Figs. S5-(b)** and **S6-(b)**). At Zr K-edge, the spectral shape of the other factor (Factor 1 in **Fig. S5-(b)**, ESI) is comparable to that of $\text{ZrO}_2(\text{t})$ (= Factor 2), but it is different from that of the comparable factor extracted for "ZC73" (**Fig. S8** in ESI). This suggests that the series of "ZC37" samples is composed of $\text{ZrO}_2(\text{t})$ and an additional phase that is structurally comparable to $\text{ZrO}_2(\text{t})$, but the additional phase differs from that found in "ZC73" samples. The same applies to the spectra collected at Ce K-edge. That is, the spectrum of the unidentified factor (Factor 2 in **Fig. S6-(b)**, ESI) is comparable to that of $\text{CeO}_2(\text{c})$ (= Factor 1) but differs from that of the comparable factor extracted for "ZC73" (**Fig. S8** in ESI). This indicates that the unidentified phase extracted for "ZC37" samples is not identical to that for "ZC73" ones.

3.2.2 EXAFS

3.2.2.1 Zr/Ce = 7/3 (ZC73)

EXAFS is more sensitive to the local structural arrangement around the absorbing atom (= speciation) than XANES.⁴² In the same manner as XANES, series of EXAFS spectra collected for "ZC73" samples were analysed by FA to extract the spectral principal factors. As shown in **Fig. S3** in ESI, the series of the EXAFS spectra can be reproduced reasonably with two principal factors both at Zr- and Ce K-edges, which is consistent with the results of XANES in 3.2.1. The series of the EXAFS spectra at Zr- and Ce K-edges and their reproductions with two principal factors are shown in **Figs. 4-(a)** and **5-(a)**, and the EXAFS spectra for the extracted two principal components and their corresponding Fourier transforms (FTs) (i.e. radial structural function: RSF) are given in **Figs. 4,5-(b)** and **-(c)**, respectively. The results of PXRD in 3.1.3 suggested that the series of the mixed Zr/Ce oxide samples are crystallographically interpreted with $\text{ZrO}_2(\text{t})$ - and $\text{CeO}_2(\text{c})$ -based phases, the pure phases of which are extracted by EXAFS-FA as one of the two principal components at Zr- and Ce K-edges, respectively (Factor 2 for Zr and Factor 1 for Ce in **Figs. 4-(b)**

and **5-(b)**). However, the fractions of these pure phases are calculated to be low, indicating that the other principal factors (i.e. Factor 1 for Zr and Factor 2 for Ce) represent the major Zr- and Ce-related phases in the samples (**Fig. 6**). At Zr K-edge, the EXAFS pattern extracted for Factor 1 is rather comparable to that for pure $\text{ZrO}_2(\text{t})$ (Factor 2) in terms of the oscillation period and wavelength (**Fig. 4-(b)**). This suggests that Factor 1 is structurally similar to Factor 2 (i.e. pure $\text{ZrO}_2(\text{t})$). Given the similarity observed in their FTs (**Fig. 4-(c)**), Factor 1 can be reasonably interpreted as the solid solution of $(\text{Zr,Ce})\text{O}_2(\text{t})$. In terms of ionic radii, Ce(IV) is larger than Zr(IV).⁴⁵ Hence, the dissolution of Ce(IV) in the $\text{ZrO}_2(\text{t})$ matrix should result in the expansion of crystal lattice of the matrix. The lattice constants of the $\text{ZrO}_2(\text{t})$ -related phase (**Table S1** in ESI) are, however, expanded only with $\sim 0.5\%$ as compared with those of pure $\text{ZrO}_2(\text{t})$ ($a = b = 3.64$ Å, $c = 5.27$ Å). This means that only a small amount of Ce(IV) in the original ZC73 mixed powder is dissolved in the $\text{ZrO}_2(\text{t})$ matrix and the majority of Ce(IV) in the original powder remains in the $\text{CeO}_2(\text{c})$ -related phase. At Ce K-edge, the EXAFS spectra of the extracted two principal factors significantly differ in oscillation pattern and amplitude (**Fig. 5-(b)**). The corresponding FTs exhibit two major peaks at $R + \Delta = 1.7$ – 1.8 and 3.3 – 3.5 Å (**Fig. 5-(c)**). Factor 1 in **Figs. 5-(b)** and **-(c)** (black data) are comparable to $\text{CeO}_2(\text{c})$, which exhibits characteristic FT peaks at $R + \Delta = 1.8$ and 3.5 Å for the nearest Ce–O and Ce–Ce arrangements in the $\text{CeO}_2(\text{c})$ structure.⁴⁶ Assuming a comparable structure arrangement between Factors 1 and 2, the FT peaks at $R + \Delta = 1.7$ and 3.3 Å observed for Factor 2 (**Fig. 5-(c)**) can be assigned as Ce–O and Ce–M (M = Ce or Zr) arrangements, respectively. Such a local structure arrangement is reasonably explained as the solid solution of $(\text{Ce,Zr})\text{O}_2(\text{c})$, which is consistent with the results of PXRD (**Table S1** in ESI). Assuming the dissolution of the smaller Zr(IV) cation into the $\text{CeO}_2(\text{c})$ matrix with larger Ce(IV) cations, the lattice constants must be shrunk. This is reasonably observed on the FTs in **Fig. 5-(c)**, where the FT peaks for Factor 2 ($(\text{Ce,Zr})\text{O}_2(\text{c})$) appear in a shorter R range than those for Factor 1 ($\text{CeO}_2(\text{c})$). Factor 2 shows a significantly smaller FT peak associated with the Ce–M arrangement ($R + \Delta = 3.3$ Å in **Fig. 5-(c)**) as compared with the corresponding peak for Factor 1, suggesting that $_{58}\text{Ce}$ atoms in Factor 2 are surrounded by a considerable number of $_{40}\text{Zr}$ atoms, the EXAFS backscattering amplitude of which is smaller than that of Ce atoms.⁴² Hence, the $(\text{Ce,Zr})\text{O}_2(\text{c})$ phase represented as Factor 2 is considered to dissolve a significant amount of Zr(IV) in the $\text{CeO}_2(\text{c})$ matrix, which is also consistent with the results of PXRD (**Table S1** in ESI).

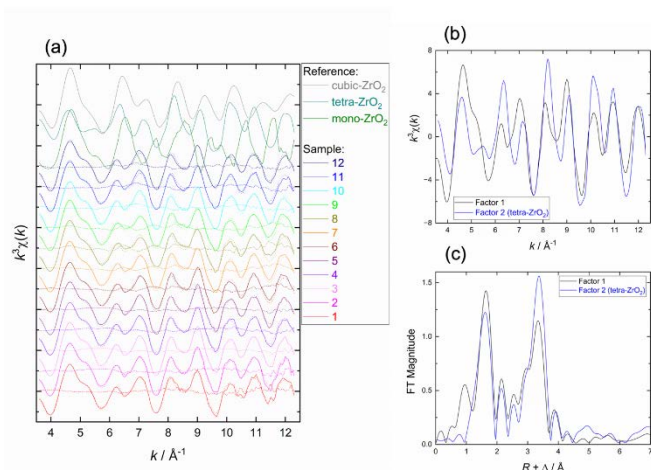


Figure 4. (a) k^3 -weighted Zr K-edge EXAFS spectra of "ZC73" samples and three reference compounds of ZrO_2 (solid lines), their reproduction by factor analysis (FA) with two principal factors (dash lines), and difference between the experimental data and FA-reproduction (dotted lines), (b) k^3 -weighted Zr K-edge EXAFS spectra of the two principal factors extracted by FA, and (c) Fourier transforms of the EXAFS spectra in (b). Phase shifts (Δ) are not corrected in (c). Sample numbers in (a) correspond to the numbers of Sample ID in Table 2.

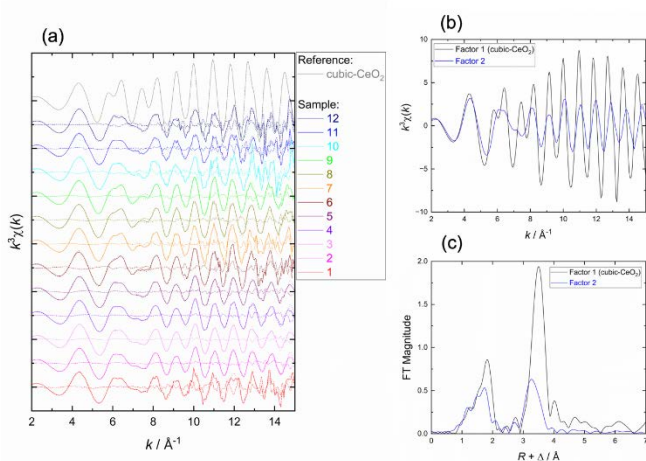


Figure 5. (a) k^3 -weighted Ce K-edge EXAFS spectra of "ZC73" samples and a reference compound of $CeO_2(c)$ (solid lines), their reproduction by factor analysis (FA) with two principal factors (dash lines), and difference between the experimental data and FA-reproduction (dotted lines), (b) k^3 -weighted Ce K-edge EXAFS spectra of the two principal factors extracted by FA, and (c) Fourier transforms of the EXAFS spectra in (b). Phase shifts (Δ) are not corrected in (c). Sample numbers in (a) correspond to the numbers of Sample ID in Table 2.

3.2.2.2 Zr/Ce = 3/7 (ZC37)

In the same manner as Section 3.2.2.1, EXAFS spectra collected for "ZC37" samples were analysed by FA, the results of which are given in Figs. 7 and 8. As is the case for "ZC73", the series of the EXAFS spectra for "ZC37" samples can be reasonably reproduced with two principal factors both at Zr- and Ce K-edges (Fig. S3 in ESI). This is also consistent with the results from XANES (Section 3.2.1). Based on the results of PXRD (Section 3.1.2), $ZrO_2(t)$ - and $CeO_2(c)$ -related phases are expected to exist in the series of "ZC37" samples (Table 1). In fact, pure $ZrO_2(t)$ - and $CeO_2(c)$ phases are extracted by FA at Zr- and Ce K-

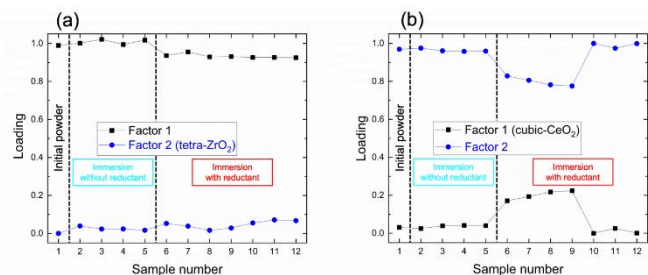


Figure 6. Variation of loading (= fraction) for the extracted two principal factors in Figs. 4 and 5 in a series of "ZC73" samples at Zr K-edge (a) and Ce K-edge (b). Mathematical errors in loading values are <1.5 and <2.2% for (a) and (b), respectively. Sample numbers correspond to the numbers of Sample ID in Table 2.

edges, respectively (Factor 2 in Fig. 7-(b) and Factor 1 in Fig. 8-(b)). The fractions of these pure oxide phases are, however, much lower than those of the other phases (i.e. Factor 1 in Fig. 7-(b) and Factor 2 in Fig. 8-(b)) (Fig. 9). This indicates that the other phases (Factor 1 for Zr K-edge and Factor 2 for Ce K-edge) are the major Zr- and Ce-containing phases. At Zr K-edge, Factor 1 extracted for "ZC37" exhibits an EXAFS oscillation pattern that is comparable to the pattern of Factor 1 for "ZC73" (Fig. 4-(b)), suggesting that Factor 1 for "ZC37" can be also interpreted as $(Zr,Ce)O_2(t)$ solid solution. However, Factor 1 for "ZC37" shows a much weaker FT peak for the Zr–M arrangement ($M = Zr$ or Ce) ($R + \Delta \approx 3.3$ Å in Fig. 7-(c)) than Factor 1 for "ZC73" (Fig. 4-(c)). Given the higher Ce content, the $(Zr,Ce)O_2(t)$ phase for "ZC37" presumably dissolves a considerable amount of Ce in the $ZrO_2(t)$ matrix. This lowers the structural order of the $ZrO_2(t)$ matrix particularly for the Zr–M arrangement and, eventually, weakens the corresponding FT peak. At Ce K-edge, the extracted two factors exhibit similar EXAFS oscillation patterns, which are comparable to that of $CeO_2(c)$ (Fig. 7-(b)). The corresponding FTs also show similar peak arrangement, although the FT peak for the Ce–M arrangement at $R + \Delta = 3.3$ Å is slightly weaker for Factor 2 than for Factor 1 (Fig. 8-(c)). Based on these facts, Factor 2 extracted at Ce K-edge is reasonably interpreted as $(Ce,Zr)O_2(c)$ solid solution. Given the higher Ce content, the $(Ce,Zr)O_2(c)$ for "ZC37" is considered to maintain the structural order of the $CeO_2(c)$ matrix, which explains the observed comparability of FT peak arrangement in Fig. 8-(c). This is also consistent with the results of PXRD, where the lattice constants calculated for the series of "ZC37" samples ($a = 5.39 \sim 5.41$ Å) are well comparable to that of pure $CeO_2(c)$ (5.41 Å). The results of phase characterization by PXRD-Rietveld and XAS-FA are summarised in Table 4.

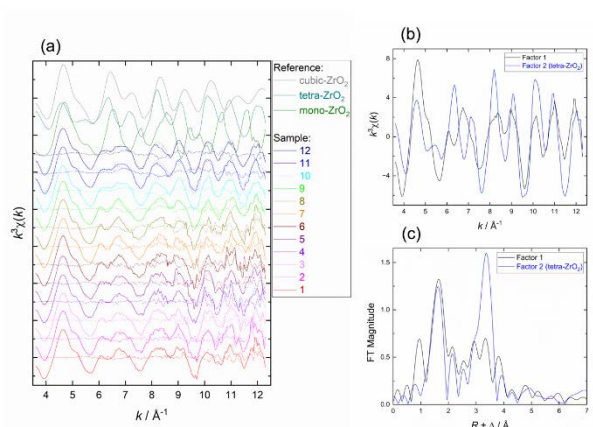


Figure 7. (a) k^3 -weighted Zr K-edge EXAFS spectra of "ZC37" samples and three reference compounds of ZrO_2 (solid lines), their reproduction by factor analysis (FA) with two principal factors (dash lines), and difference between the experimental data and FA-reproduction (dotted lines), (b) k^3 -weighted Zr K-edge EXAFS spectra of the two principal factors extracted by FA, and (c) Fourier transforms of the EXAFS spectra in (b). Phase shifts (Δ) are not corrected in (c). Sample numbers in (a) correspond to the numbers of Sample ID in Table 3.

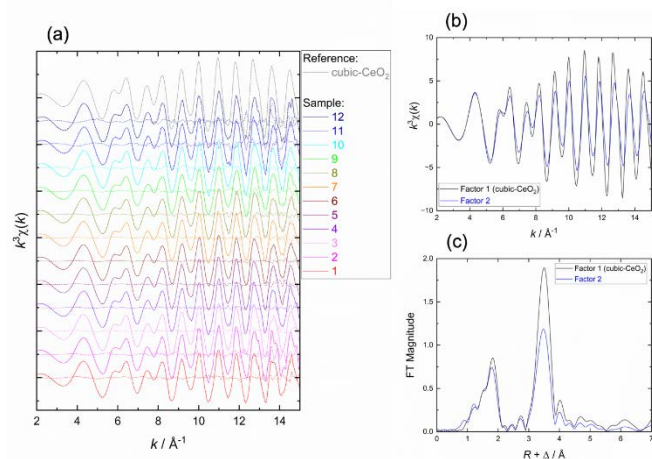


Figure 8. (a) k^3 -weighted Ce K-edge EXAFS spectra of "ZC37" samples and a reference compound of $CeO_2(c)$ (solid lines), their reproduction by factor analysis (FA) with two principal factors (dash lines), and difference between the experimental data and FA-reproduction (dotted lines), (b) k^3 -weighted Ce K-edge EXAFS spectra of the two principal factors extracted by FA, and (c) Fourier transforms of the EXAFS spectra in (b). Phase shifts (Δ) are not corrected in (c). Sample numbers in (a) correspond to the numbers of Sample ID in Table 3.

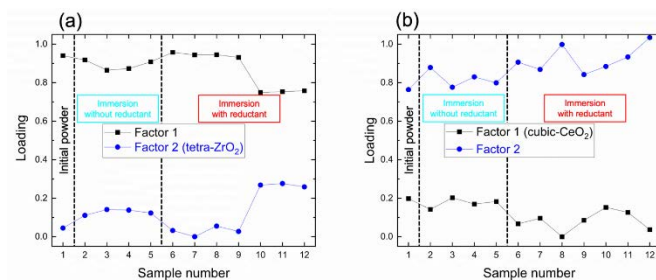


Figure 9. Variation of loading (= fraction) for the extracted two principal factors in Figs. 7 and 8 in a series of "ZC37" samples at Zr K-edge (a) and Ce K-edge (b). Mathematical errors in loading values are <2.2 and <2.1% for (a) and (b), respectively. Sample numbers correspond to the numbers of Sample ID in Table 3.

Table 4 Summary of solid phase characterization by PXRD-Rietveld analysis and XAS-FA

		ZC73		ZC37	
		Major	Minor	Major	Minor
PXRD-Rietveld	As synthesised	(Zr,Ce)O ₂ (t)	(Ce,Zr)O ₂ (c)	(Ce,Zr)O ₂ (c)	(Zr,Ce)O ₂ (t)
	Immersion w.o. reductant	(Zr,Ce)O ₂ (t)	(Ce,Zr)O ₂ (c)	(Ce,Zr)O ₂ (c)	(Zr,Ce)O ₂ (t)
	Immersion with reductant	(Zr,Ce)O ₂ (t) (decrease)	(Ce,Zr)O ₂ (c) (increase)	(Ce,Zr)O ₂ (c)	(Zr,Ce)O ₂ (t) (increase)
XAS-FA	As synthesised	(Zr,Ce)O ₂ (t)	(Ce,Zr)O ₂ (c)	(Ce,Zr)O ₂ (c)	(Zr,Ce)O ₂ (t)
	Immersion w.o. reductant	(Zr,Ce)O ₂ (t)	(Ce,Zr)O ₂ (c)	(Ce,Zr)O ₂ (c)	(Zr,Ce)O ₂ (t)
	Immersion with reductant	(Zr,Ce)O ₂ (t)	(Ce,Zr)O ₂ (c), CeO ₂ (c)	(Ce,Zr)O ₂ (c) (increase)	(Zr,Ce)O ₂ (t) (increase)

3.3 Solubility measurement

3.3.1 Solubility of cerium from pure CeO₂

The solubility of Ce from pure CeO₂ was investigated with different forms of CeO₂, that is, CeO₂ synthesised in this study (= ZC010, 88 nm in particle size determined by PXRD-Rietveld), commercial normal powder (84 nm) and nanopowder (22 nm) of CeO₂. SEM observation suggested that the CeO₂ powder synthesised in this study possesses porous structure which is presumably formed via the decomposition and volatilization of PVA during the heating process (Fig. S8 in ESI). Figure 10 shows the measured solubility of Ce from the three CeO₂ powders under an atmospheric condition without SnCl₂ (i.e. reductant), together with the solubility reported for nanocrystalline CeO₂ (5.7 nm).⁴⁷ In terms of solubility and its variation with pH_c, ZC010 is comparable to the normal CeO₂ powder, whilst the solubility of CeO₂ nanopowder is higher than those for ZC010 and the normal CeO₂ powder in the whole pH_c range. The nanocrystalline CeO₂ shows farther higher solubility than the CeO₂ nanopowder particularly in the acidic region. Given their particle sizes, these results suggest that the measured "apparent" solubility increases with decreasing the particle size. That is, the higher the surface area (= the smaller the particle size) becomes, the more the CeO₂ phase is dissolved. For the samples used for the solubility measurements, the pH_c and Eh values were also measured (Fig. S10 in ESI). As mentioned in detail in Section 5 of ESI, the solubility of Ce (i.e. the total concentration of Ce dissolved in the system: [Ce]_{tot}) can be thermochemically calculated based on pH_c and Eh, the result of which is shown in Fig. 10. The thermochemical solubility ([Ce]_{tot}: the solid line in Fig. 10) is calculated to be much higher than the measured "apparent" solubility (the plotted data in Fig. 10). This difference between the calculated and experimental solubility presumably stems from dissolution kinetics.⁴⁸ Thermochemical calculation indicates that the dissolved form of Ce in the system is Ce(III) cations (Fig. S10 in ESI). The reductive dissolution of Ce from Ce^{IV}O₂(s) to form Ce(III) cations in solution is kinetically slow⁴⁸ and it is significantly affected by the surface area of CeO₂(s). This means that the larger the surface area (the smaller the particle size) is, the faster the dissolution is and, consequently, the larger the apparent solubility becomes. The observed decreasing tendency of the "apparent" solubility with increasing the particle size is well consistent with this hypothesis. This also implies that, if the solubility measurement is performed for much longer duration, the apparent solubility approaches to the thermodynamically calculated solubility.

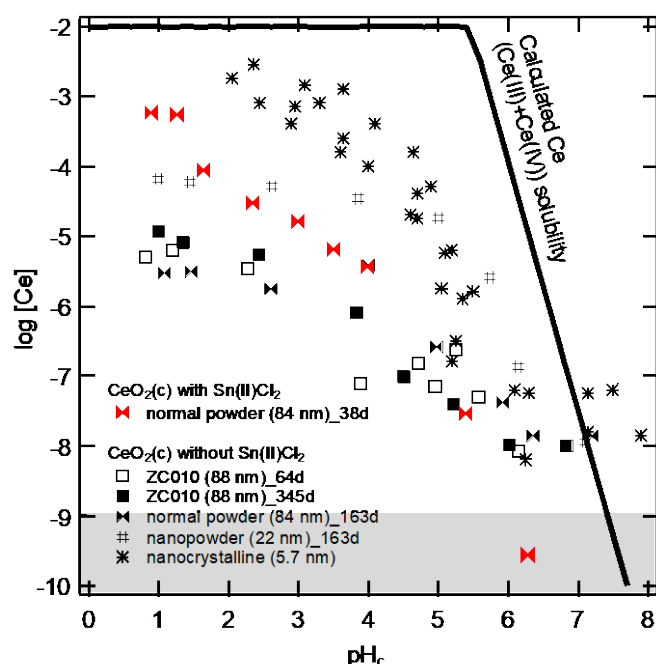


Figure 10. Solubility of cerium from CeO₂ with different particle size. The solubility of nanocrystalline CeO₂ (5.7 nm) is taken from Plakhova et al.⁴⁷ The solid line represents the thermodynamically calculated solubility ([Ce]_{tot}), the details of which are given in Section 5 of ESI. The grey area in the figure (bottom) indicates the detection limit of ICP-MS employed in this study.

The dissolution behaviour of CeO₂ changes when the reductant (SnCl₂) is added to the system. That is, the addition of the reductant results in more than 10 times higher "apparent" solubility as compared with the solubility without the reductant (Fig. 10). Since the thermodynamic equilibrium for the dissolution of CeO₂(s) (i.e. [Ce]_{tot}) is not significantly affected by the presence of SnCl₂, it is reasonable to consider the observed increase in "apparent" solubility as a result of the change in dissolution kinetics. That is, the addition of SnCl₂ accelerates the reduction of Ce(IV) to - (III) in solution, which is kinetically slow⁴⁹ and one of the rate-determining reactions in the dissolution of CeO₂(s).⁴⁸ This eventually quickens the overall dissolution kinetics to give higher "apparent" solubility, although it is still lower than the thermodynamically calculated solubility ([Ce]_{tot}).

3.3.2 Solubility of cerium from "Zr/Ce oxide s.s."

The solubility of Ce from "Zr/Ce oxide s.s." (i.e. ZC73 and -37) was investigated under the same solution condition employed for the measurement with pure CeO₂ (Section 3.3.1). As summarised in

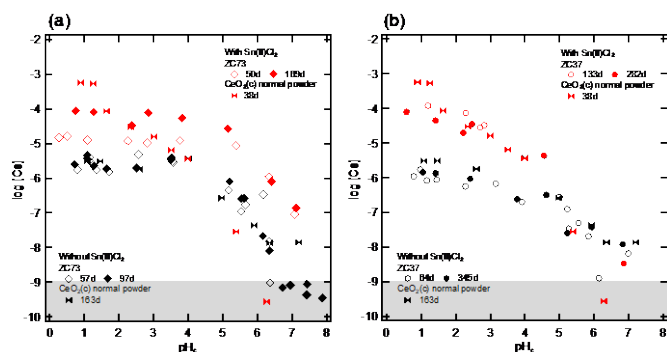


Figure 11. Solubility of cerium from ZC73 (a) and ZC37 (b) together with the solubility from normal powder of CeO_2 (84 nm in particle size). The grey area in the figure (bottom) indicates the detection limit of ICP-MS employed in this study.

Table 4, the major phases for ZC73 and -37 are $(\text{Zr,Ce})\text{O}_2(\text{t})$ and $(\text{Ce,Zr})\text{O}_2(\text{c})$, respectively. These phases are expected to be the dominant phases controlling the dissolution mechanism and kinetics. The measured "apparent" solubility for ZC73 and -37 was given in **Figs. 11-(a)** and **-(b)**, respectively. In the absence of the reductant, the solubility from "Zr/Ce oxide s.s." is comparable to that from pure CeO_2 (normal powder), suggesting a comparable mechanism of Ce dissolution from "Zr/Ce oxide s.s." and pure CeO_2 . This also indicates that, for ZC73, the dissolution of Ce presumably occurs from the minor phase of $(\text{Ce,Zr})\text{O}_2(\text{c})$, which is comparable to pure $\text{CeO}_2(\text{c})$. Additionally, the solubility is not affected by immersion duration (black square plots in **Fig. 11-(a)** and black circle plots in **Fig. 11-(b)**), indicating the slow dissolution kinetics observed for the pure CeO_2 system (**Section 3.3.1**).

The situation changes when the reductant is added to the system. That is, the solubility from "Zr/Ce oxide s.s." becomes one to two orders of magnitude larger than the solubility without the reductant in the whole pH_c range. When comparing the results for ZC73 and -37 with the reductant (i.e. red plots in **Fig. 11**), the solubility for ZC73 deviates significantly from that for pure CeO_2 (**Fig. 11-(a)**), whilst the solubility for ZC37 is fairly comparable to that for pure CeO_2 (**Fig. 11-(b)**). It should be also noted that the solubility for ZC73 increases with immersion duration in the acidic range of $\text{pH}_c < 5$, whilst there is no significant effect of immersion duration on the solubility for ZC37. These results indicate that the mechanism and kinetics of Ce dissolution differ between ZC73 and -37, which is reasonable given the major phases in "Zr/Ce oxide s.s." (i.e. $(\text{Zr,Ce})\text{O}_2(\text{t})$ for ZC73 and $(\text{Ce,Zr})\text{O}_2(\text{c})$ for ZC37) (**Table 4**). As shown in **Fig. 11**, the solubility of Ce decreases with increasing pH over $\text{pH} = 5$, where the lattice constants of the $\text{CeO}_2(\text{c})$ phase change (Tables S1 and S2 in ESI). This implies that the observed decreasing tendency of Ce solubility around $\text{pH} = 5$ may relate to the structural change of the $\text{CeO}_2(\text{c})$ phase in the samples.

3.3.3 Solubility of zirconium from "Zr/Ce oxide s.s."

In general, zirconium oxide (ZrO_2) is considered to be insoluble in water.¹¹ The cationic aqueous species of Zr (Zr(IV)(aq)) hydrolyse very strongly to form hydrolytic precipitate immediately.¹¹ For these reasons, the solubility of Zr is expected to be extremely low. Nonetheless, the solubility of Zr from "Zr/Ce oxide s.s." was measured in the same manner as **Section 3.3.2**. As shown in **Fig. 12**, the measured solubility of Zr was almost constant with $[\text{Zr}] = 10^{-8}$ mol/L above $\text{pH}_c = 1$, and it increases in the strongly acidic region below $\text{pH}_c = 1$. This is in good agreement with the solubility

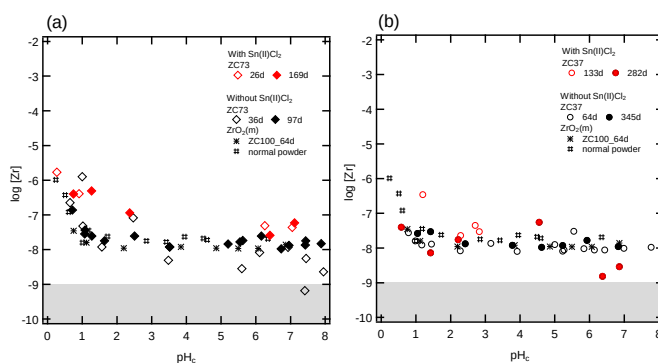


Figure 12. Solubility of zirconium from ZC73 (a) and ZC37 (b) together with the solubility from reagent-grade $\text{ZrO}_2(\text{m})$ (normal powder) reported in Kobayashi et al.⁵⁰ The grey area in the figure (bottom) indicates the detection limit of ICP-MS employed in this study.

determined for reagent-grade $\text{ZrO}_2(\text{m})$.⁵⁰ The addition of the reductant (SnCl_2) does not result in significant increase in the Zr solubility, which was observed in the Ce solubility. Based on the results in **Section 3.3.2**, approximately 1 mol% of Ce in ZC73 was dissolved in solution at $\text{pH}_c < 5$ in the presence of the reductant. However, the measured solubility of Zr indicates that only ~ 0.01 mol% of Zr in ZC73 was dissolved in solution under the same condition. The same applies to ZC37. Hence, the dissolution of "Zr/Ce oxide s.s." is apparently heterogeneous and the dissolution mechanism/kinetics differs between Ce and Zr.

4 Discussion

As summarised in **Table 4**, the results of PXRD-Rietveld and XAS-FA indicate that the initial major phases of ZC73 and -37 are $\text{ZrO}_2(\text{t})$ -based solid solution of $(\text{Zr,Ce})\text{O}_2(\text{t})$ and $\text{CeO}_2(\text{c})$ -based solid solution of $(\text{Ce,Zr})\text{O}_2(\text{c})$, respectively, whilst the minor phases are the opposite (i.e. $(\text{Ce,Zr})\text{O}_2(\text{c})$ for ZC73 and $(\text{Zr,Ce})\text{O}_2(\text{t})$ for ZC37). In terms of the pure oxides of Zr(IV) and Ce(IV), $\text{ZrO}_2(\text{m})$ and $\text{CeO}_2(\text{c})$ are the most stable phases under a normal condition (i.e. at room temperature with ambient pressure). Based on the solubility products (K_{sp}), $\text{CeO}_2(\text{c})$ is three orders of magnitude more soluble than $\text{ZrO}_2(\text{m})$ ($\log K_{\text{sp}} = -59.3$ and -62.5 for $\text{CeO}_2(\text{c})$ and $\text{ZrO}_2(\text{m})$, respectively),^{47, 50} (**Section 5** in ESI) which was also demonstrated in **Figs. 10** and **12**. When comparing the monoclinic- and tetragonal phases, $\text{ZrO}_2(\text{m})$ is thermodynamically and structurally more stable than $\text{ZrO}_2(\text{t})$, but its difference is expected to be rather slight.⁵¹ Additionally, depending on the grain size and addition of dopants (e.g. CeO_2), the stability of the monoclinic- and tetragonal phases can be reversed.^{52, 53} Given these facts, $\text{ZrO}_2(\text{t})$ is expected to be as hardly soluble as $\text{ZrO}_2(\text{m})$ and, therefore, the order of solubility is expected to be $\text{CeO}_2(\text{c}) \gg \text{ZrO}_2(\text{t}) \approx \text{ZrO}_2(\text{m})$. This suggests that the $(\text{Ce,Zr})\text{O}_2(\text{c})$ phase dominates the dissolution of "Zr/Ce oxide s.s." over the $(\text{Zr,Ce})\text{O}_2(\text{t})$ one. Hence, the observed solubility in **Figs. 11** and **12** is considered to arise mainly from the $(\text{Ce,Zr})\text{O}_2(\text{c})$ phase in "Zr/Ce oxide s.s."

As demonstrated in **Figs. 11** and **12**, the solubility of "Zr/Ce oxide s.s." is governed by the dissolution of Ce, which is enhanced by the addition of a reductant. It is obvious that the reductant (Sn(II)) reduces Ce(IV) to $-\text{(III)}$, whilst it does not affect the chemical status of redox-inert Zr(IV) . Given these facts, two possible scenarios can be considered in terms of the role of the reductant in the dissolution of "Zr/Ce oxide s.s.". The first scenario is based on the dissolution of

Ce(IV) from the (Ce,Zr)O₂(c) phase in "Zr/Ce oxide s.s.", which is followed by the reduction of the dissolved Ce(IV) species to -(III) ones in solution. In this first scenario, the reductant plays its role only in the solution phase. On the other hand, in the second scenario, the reductant acts on Ce(IV) at the solid surface to generate Ce(III) retained in the solid phase. This reduction induces structural rearrangement at the solid phase surface, eventually triggering the dissolution of Ce into the solution phase. The results of PXRD and XAS indicate that "Zr/Ce oxide s.s." undergoes structural change when immersing with the reductant. Although the first scenario would also involve structural rearrangement of the solid phase as a result of the separation of Ce from the solid phase, the structural rearrangement in the second scenario is expected to be more significant. Hence, "the reduction of Ce at the solid phase surface" is a more likely scenario for the dissolution of "Zr/Ce oxide s.s." in the presence of a reductant.

When considering the observed solubility of Ce from "Zr/Ce oxide s.s.", the maximum solubility was $[Ce] = \sim 10^{-4}$ mol/L (Fig. 11). This corresponds to ca. 3.3 and 1.4 mol% of Ce in ZC73 and -37 solid samples, respectively, and two orders of magnitude smaller than the thermodynamically calculated solubility ($[Ce]_{\text{tot}}$) (Fig. 10). This inconsistency between the observed and thermodynamically calculated solubility could be interpreted as a result of the formation of a protective layer at the solid phase surface. Assuming the second dissolution scenario, Ce(IV) in the (Ce,Zr)O₂(c) phase is reduced to Ce(III) by the reductant and then dissolved into solution. This, in another respect, increases the Zr content in the (Ce,Zr)O₂(c) remaining at the surface, which could further induce phase transformation from cubic- to tetragonal/monoclinic phases.⁴⁰ This is consistent with the results of PXRD-Rietveld and XAS-FA (Table 4). Since the tetragonal/monoclinic phases are more stable than the cubic one, the newly formed tetragonal/monoclinic phases at the surface can act as a protective layer that restrains further dissolution of "Zr/Ce oxide s.s.". The decrease of the Ce content at the surface lowers the efficacy of the reductant, also hindering the dissolution of "Zr/Ce oxide s.s." surface.

A recent study on the dissolution of oxide solid solution composed of trivalent lanthanides reported that, when the oxide solid solution was soaked in an aqueous solution (0.1 mol/L NaClO₄ at neutral-alkaline pH), the hydroxide solid solution of the original lanthanides is formed.⁵⁴ Such hydroxide solid solution is not formed when a simple mixture of the corresponding pure lanthanide oxides is immersed,⁵⁴ suggesting that the dissolution of metal components in oxide solid solution can occur simultaneously. The same scenario can apply to the present case of "Zr/Ce oxide s.s.". That is, the Zr and Ce components of "Zr/Ce oxide s.s." possibly dissolves simultaneously. The dissolved Ce species could be already reduced to Ce(III) in the solid phase, otherwise they are immediately reduced to Ce(III) in the presence of a reductant. Part of the resultant Ce(III) species further hydrolyses to form hydroxide Ce(III) species at the surface. These Ce(III) hydroxide species are, however, transformed to CeO₂ upon drying (Section 6 in ESI). As compared with trivalent lanthanides (including Ce(III)), the hydrolysis of Zr(IV) is significantly stronger and the hydrolysis products are easily transformed to ZrO₂(m/t) also upon drying.⁵⁵⁻⁵⁷ This hypothesis reasonably explains the observed changes in lattice parameters (Fig. 3) and increased fractions of pure ZrO₂(t) and CeO₂(c) phases (Figs. 6-(b) and 9-(a)) after the immersion with the reductant. In contrast to the combination of trivalent lanthanides, there is a huge difference in the degree of hydrolysis between Zr(IV) and Ce(III),^{11, 58} which is presumably the reason why the hydroxide solid solution of Zr(IV) and Ce(III) was not formed in the present study.

5 Conclusion

This study investigated the dissolution behaviour of the oxide solid solution containing Zr and Ce (i.e. "Zr/Ce oxide s.s."). The dissolution is dominated by the release of the Ce component. The dissolution is further enhanced with the addition of a reductant presumably *via* the reduction of Ce(IV) to -(III), inducing structural rearrangement at the surface of the solid state to form a more soluble phase. This newly formed soluble phase at the surface is protected by the subsequently formed less soluble layer, e.g. ZrO₂(t). This hypothetical dissolution mechanism is well consistent with the results of solid-phase characterization by PXRD and XAS, as well as those from solubility measurements.

This study also demonstrates the complex dissolution behaviour of the solid solution containing redox-active metals. That is, owing to significant difference in their redox and hydrolysis/complexation behaviour, the redox and dissolution reactions of the metal components do not occur homogeneously, resulting in heterogeneous dissolution of the metal components and formation of less soluble phases at the surface to restrain further dissolution of the solid phase. Such solid solution systems containing redox-active metals would be more relevant to the actual technological/industrial materials and natural minerals associated with the SSAS system. For instance, as mentioned in Introduction, MOX and spent nuclear fuels contain the oxide solid solution containing multiple redox-active actinides. The solid solution containing redox-active transition metals (e.g. Cr, Mn, Fe, etc.) can be easily found in natural minerals. The multi-technique approach employed in this study is one of the powerful ways to gain deeper mechanistic insight into the chemistry on such solid solution systems with redox-active metals.

Author contributions

TK: funding acquisition, conceptualisation, PXRD data analysis, and major manuscript writing. YS: sample preparation, PXRD and solubility experiments. RT: solubility data analysis, visualisation. DM: XAS data acquisition. TS: visualisation, supervision. AIO: conceptualisation, XAS data analysis, visualisation, and major manuscript writing and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant-in-Aid for Scientific Research B, 2020–2023, No. 20H02664). Synchrotron radiation experiments were performed at SPring-8 with approval of Japan Atomic Energy Agency (JAEA) (Proposal No. 2021B-E02). XAS data of ZrO₂(t) and -(c) were provided by courtesy of Dr. Christoph Hennig at HZDR/ESRF, which is highly appreciated.

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(Table data)

Table 1 Summary of "Zr/Ce oxide s.s." samples with different Zr/Ce molar ratios

Sample ID	Zr/Ce molar ratio	Solution condition for immersion in 0.5 mol/L NaClO ₄	
		pH _c	Reductant (SnCl ₂)
ZC37-1 (= ZC37)	3 / 7	(without immersion)	
ZC37-2		0.89	None
ZC37-3		3.07	
ZC37-4		5.14	
ZC37-5		6.42	
ZC37-6		1.20	Added
ZC37-7		2.29	
ZC37-8		2.71	
ZC37-9		2.83	
ZC37-10		4.99	
ZC37-11		6.55	
ZC37-12		6.85	

Table 2 Summary of "Zr/Ce oxide s.s." samples (70 mol%-Zr: ZC73)) for immersion experiments

Sample ID	Zr/Ce molar ratio	Solution condition for immersion in 0.5 mol/L NaClO ₄	
		pH _c	Reductant (SnCl ₂)
ZC73-1 (= ZC73)	7 / 3	(without immersion)	
ZC73-2		1.08	None
ZC73-3		3.52	
ZC73-4		6.16	
ZC73-5		7.44	
ZC73-6		1.20	Added
ZC73-7		2.25	
ZC73-8		2.51	
ZC73-9		2.83	
ZC73-10		3.96	
ZC73-11		6.41	
ZC73-12		7.20	

Table 3 Summary of "Zr/Ce oxide s.s." samples (30 mol%-Zr: ZC73)) for immersion experiments

Sample ID	Zr/Ce molar ratio
ZC100	10 / 0
ZC91	9 / 1
ZC73	7 / 3
ZC55	5 / 5
ZC37	3 / 7
ZC19	1 / 9
ZC010	0 / 10