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# The effect of dopants on the redox performance, microstructure and phase formation of ceria



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# HIGHLIGHTS

• Sintering, microstructure and redox performance of doped ceria are investigated.

• Solid state reaction and Pechini synthesis yield qualitatively equal samples.

Grain growth of CeO<sub>2</sub> is decreased by doping with HfO<sub>2</sub>, ZrO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub> and Li<sub>2</sub>O-HfO<sub>2</sub>.
Pores can be effectively retained at high temperatures Li by co-doping.

Oxygen exchange capacity of ceria is dramatically increased with Zr and Hf doping.

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### ABSTRACT

A solid state reaction is employed to investigate the influence of  $ZrO_2$ ,  $HfO_2$ ,  $Pr_6O_{11}$ ,  $TiO_2$  and  $Li_2O$  doping on  $CeO_2$  for a possible use in solar thermochemical redox cycles. Ceramics with a macroscopic interconnected porosity, necessary for high mass transport during redox cycles, are produced by the addition of spherical carbon particles prior to sintering. Partial closure of porosity is detectable when  $CeO_2$  is doped with Pr, Zr or Hf, while Li co-doping retains interconnected porosity more effectively than other doped or pristine ceria samples. In dense ceramics, microstructures reveal a reduction of the average grain size of pristine  $CeO_2$  with increasing Zr and Hf dopant concentration. These trends are validated using Pechini synthesized materials of the same composition. The reduction in grain size is even more pronounced for Pr doped  $CeO_2$  and Li doped  $Hf_{0.1}Ce_{0.9}O_2$ , while TiO<sub>2</sub> doping induces softening of samples under operating conditions (>1500 °C) limiting its use for high temperature applications. The redox performance of  $M_xCe_{1-x}O_{2-\delta}$  (M = Zr, Hf;  $0 \le x \le 0.2$ ) can be increased significantly with increasing Zr and Hf dopant concentration. At x = 0.2 (Zr, Hf) the fuel production rates are doubled as compared to pristine  $CeO_2$ . The redox performance of Hf doped  $CeO_2$  remains stable upon co-doping with Li<sup>+</sup>.

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# 1. Introduction

Thermochemical redox cycles make use of concentrated solar energy to split  $CO_2$  and  $H_2O$  and produce syngas  $(CO/H_2)$  [1]. A variety of redox pairs can be utilized to perform the redox reactions,

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including Fe<sub>3</sub>O<sub>4</sub>/FeO, Mn<sub>3</sub>O<sub>4</sub>/MnO, Co<sub>3</sub>O<sub>4</sub>/CoO, and ZnO/Zn ([1–3] and literature cited therein), LaSrMO<sub>3- $\delta$ </sub> (M = Mn, Co, Cr)-based perovskites [4–7], and CeO<sub>2</sub>-based materials [8–13]. Perovskites show promising reaction yields but phase transitions at high temperatures and reactivity of La and Sr towards CO<sub>2</sub> remain limiting factors. In this context, cerium dioxide is promising especially due to its high temperature phase stability under reducing conditions [9,10,14]. Solar thermochemical fuel production based on CeO<sub>2</sub> proceeds via the following two steps: 1) a (solar) endothermic reduction of ceria at temperatures of ~1500 °C (Eq. (1))

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$$CeO_2 \to CeO_{2-\delta} + \frac{\delta}{2}O_2 \tag{1}$$

where  $\delta$  denotes the oxygen nonstoichiometry; and 2) the (nonsolar) reaction of reduced CeO<sub>2- $\delta$ </sub> with CO<sub>2</sub> (Eq. (2)) and H<sub>2</sub>O (Eq. (3)) at lower temperatures (~1000 °C) to produce syngas.

$$CeO_{2-\delta} + \delta CO_2 \to CeO_2 + \delta CO \tag{2}$$

$$CeO_{2-\delta} + \delta H_2 O \rightarrow CeO_2 + \delta H_2$$
 (3)

Stoichiometric CeO<sub>2</sub> is regained and the redox cycle is closed [11,15]. The syngas (CO/H<sub>2</sub>) gained during the oxidation reaction Eq. (2) and (3) can be catalytically converted into liquid hydrocarbons. Recently, the first ever production cycle of jet-fuel (solar-to-syngas-to-kerosene) has been demonstrated by Marxer et al. using a 4 kW solar reactor prototype where 291 stable solar-driven redox cycles were performed that yielded 700 standard liters of syngas [9].

The efficiency of the redox cycle is driven by two major factors: The nonstoichiometry  $\delta$  gained during reduction and the kinetics of the reduction and oxidation reaction. First of which determines the maximum amount of CO/H<sub>2</sub> produced *per* cycle while the latter determines the quantity of fuel produced over time. Numerous investigations aim at increasing the nonstoichiometry  $\delta$ , also referred to as oxygen exchange capacity, by means of doping. In the relevant temperature range ( $\geq 1500 \,^{\circ}$ C) M<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub> (M = Ti, Hf, Zr, Pr) solid solutions synthesized by wet-chemical methods have demonstrated promising RedOx behavior [16–21].

Doping of CeO<sub>2</sub> (r(Ce<sup>4+</sup>) = 0.97 Å) with smaller isovalent Zr<sup>4+</sup> (0.84 Å), Hf<sup>4+</sup> (0.83 Å) or Ti<sup>4+</sup> (0.78 Å) cations can increase the achievable nonstoichiometry  $\delta$  significantly. This is attributed to a contraction of the ceria lattice upon substitution of the host Ce<sup>4+</sup> cation with smaller isovalent cations [10,18,22]. By a distortion of the oxygen sublattice some metal – oxygen bonds are strengthened, while others are weakened, creating a higher driving force for the creation of 7-fold coordinated metal-sites and subsequently the release of O<sub>2</sub> [23]. Despite the different valence a different mechanism has been suggested for Li<sup>+</sup> (0.92 Å) doping [24].

Solid solutions of  $Pr_xCe_{1-x}O_{2-\delta}$  were effective in promoting the  $O_2$  release and  $H_2$  production in thermochemical water splitting reactions [19]. For Pr doping the enhanced reactivity was ascribed to the chemical similarity between cerium oxides and praseodymium oxides having a promotional effect on the redox performance of ceria.

Experiments in a solar reactor with a load of 1.5 kg of undoped CeO<sub>2</sub> have shown that, by adding a carbon pore forming agent prior to sintering, the introduction of an interconnected pore structure in the  $\mu$ m-range significantly increased the redox performance [25]. Accordingly, retaining the interconnected pore structure at high temperatures is of significant interest for the redox performance. The use of nanometer sized powders would not allow for a retainment of interconnected porosity during high temperature operation (>1500 °C) due to a high sintering activity owing to high surface energies. Using  $\mu$ m-sized oxide powders, and thus classical solid state reaction routes, will reduce sintering effects and allow for the formation of structures with sufficient microstructural stability at operating temperatures of ~1500 °C, hereafter referred to as microstructural stability [8,15,25].

In this study we describe the synthesis of doped ceria using a solid state reaction method. Doping of a µm-sized ceria powder with nm-sized oxide dopants Zr, Hf, Pr and Ti, and co-doping of Hf<sub>x</sub>Ce<sub>1-x</sub>O<sub>2- $\delta$ </sub> with Li is investigated. The synthesis involves only wet-milling and drying, low pressure compaction and a single sintering step.

The influence of type and concentration of dopants on the sintering properties is discussed. The microstructural and phase development after a single sintering step (1600 °C, 5 h) are compared to equivalent samples prepared by a wet-chemical Pechini synthesis, which provides a more homogeneous dopant distribution on an atomic scale. Finally, the redox properties of samples synthesized by solid state reaction are investigated using thermogravimetric analysis to examine the influence of dopants on the achievable nonstoichiometry  $\delta$  and fuel (H<sub>2</sub>/CO) production properties.

# 2. Experimental

#### 2.1. Solid state reaction of doped ceria

Solid solutions of  $M_xCe_{1-x}O_{2-\delta}$  (M = Ti, Hf, Zr, Pr; x = 0.05, 0.1, 0.15, 0.2) were synthesized using CeO<sub>2</sub> (Sigma Aldrich, 99.9%) and stoichiometric amounts of TiO<sub>2</sub> (P25 Degussa), HfO<sub>2</sub> (Alfa Aesar, 99.95%), ZrO<sub>2</sub> (TZ-0, 99.95%, Tosoh, Japan) and Pr<sub>6</sub>O<sub>11</sub> (Alfa Aesar, 99.99%) powders (particle sizes listed in Table 1). Co-doping with 2-, 6- and 10 mol – % Li<sup>+</sup> was carried out on Hf<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2- $\delta$ </sub> by addition of Li<sub>2</sub>CO<sub>3</sub> (Alfa Aesar, 99.998%).

Deagglomeration and mixing of the metal oxides was carried out by ball milling on a roller mill (ZOZ, RM1, Germany) for 24 h in polypropylene bottles using yttria-stabilized zirconia balls of 5 mm diameter (Tosoh, Japan) and distilled water. After 24 h the slurry was separated from the YSZ balls and dried at 85 °C during 12 h. Samples of 300 mg were uniaxially pressed at 5 MPa in a 10 mm pressing die. Porous samples were produced using the same powder precursors and adding carbon pore forming (CPF) particles (0.4-12 µm, HTW Hochtemperatur Werkstoffe GmbH) in a 1:1 volume ratio (5:1 mass-ratio) of ceramic powder:CPF. All samples were sintered (Carbolite HTF 17/10) under the same conditions at 1600 °C for 5 h. They were placed on an alumina plate and a ceria powder bed to avoid reaction between samples and the alumina plate during sintering. Porous samples were used for thermogravimetric analysis while phase development, microstructure and sintering properties were investigated using dense samples.

# 2.2. Pechini synthesis of doped ceria

The Zr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub> and Hf<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub> ( $0 \le x \le 0.2$ ) solid solutions were synthesized from a polymerized complex method (Pechini synthesis). (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (Alfa Aesar, 99.9%) and ZrO(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar, 99.9%) or HfCl<sub>4</sub> (Alfa Aesar, 99.9%) were stoichiometrically mixed and dissolved in deionized water. Anhydrous citric acid (CA) (Sigma–Aldrich, 99.5%) was added to 1,4-butanediol (BD) (Sigma–Aldrich, 99%) in a 1:4 molar ratio (with [CA]:[M<sup>4+</sup>] = 4:1) and stirred at 100 °C until all citric acid was dissolved. The aqueous solution containing the dissolved metal salts was added to the CA-BD mixture and heated to 150 °C to promote the esterification reactions. The resulting highly viscous polymer was dried at 80 °C for 24 h and fired for 10 h at 700 °C in a constant air flow to remove

 Table 1

 Particle sizes of the metal oxides used for the solid state reaction synthesis derived from <sup>(1)</sup>SEM images or <sup>(2)</sup>supplier information.

Material	Particle size
CeO <sub>2</sub>	1 μm <sup>(1)</sup>
ZrO <sub>2</sub>	70 nm <sup>(2)</sup>
HfO <sub>2</sub>	<250 nm <sup>(1)</sup>
$Pr_6O_{11}$	<1 µm (acicular) <sup>(1)</sup>
TiO <sub>2</sub>	21 nm <sup>(2)</sup>

organics. The samples were mortared and pressed uniaxially at 5 MPa in a 10 mm pressing die and sintered for 5 h at 1600  $^\circ C$  as described above.

# 2.3. Sample characterization

Phase development and lattice parameters were determined by x-ray diffraction (XRD), recorded on a Bruker D8 diffractometer (Parallel Beam) with Cu-K $\alpha$  radiation in a 2 $\theta$  range of 10–110° (step size 0.014°, scan speed 1°/min). Rietveld refinement was done using the Bruker Topas 4.2 software and stoichiometric CeO<sub>2</sub> (ICSD 72155) as structural model. The unit cell parameters, zero corrections, scaling factors, peak shape (Pseudo-Voigt profile functions, including FWHM (*W*)), isotropic thermal factors, atomic coordinates and site occupancies were refined in the given order. Ionic radii were used from Shannon et al. [26].

The microstructural development was examined using scanning electron microscopy (SEM). Bulk samples were embedded in epoxy resin, ground using 30  $\mu$ m diamond discs and polished (Buhler, PHOENIX 4000) with diamond suspension (MetaDi, Bühler) from 15  $\mu$ m down to 1  $\mu$ m. The samples were thermally etched at 1500 °C for 30 min to reveal the grain boundaries. After sputtering with Au/Pd, scanning electron microscopy (SEM, FEI ESEM XL30) was performed using high-vacuum secondary electron (SE) and back-scattered electron (BSE) detectors. Average grain sizes were determined for at least 100 but typically >250 grains in SEM micrographs using an image analysis software package (Image], 1.47v).

The 2D porosity of sintered porous samples was determined following a similar procedure to that employed for the examination of the microstructures, but omitting the thermal etching step. The porous ceramic samples were infiltrated with an epoxy resin under pressure [Kulzer, Technomat] for 12h followed by cutting, grinding and polishing of the sample. Infiltrated pores can be distinguished from bulk ceramic and non-infiltrated pores by their lower back-scattering index in SEM. The area of filled pores (black) and the bulk material (white) was calculated applying a thresholding technique (ImageJ, 1.47v).

The sintering behavior of doped and undoped ceria was investigated using push-rod dilatometry (Baehr, DIL-802) with cylindrical samples of  $\emptyset = 5$  mm and 10 mm length. The heating rates applied were 5 °C/min for heating and cooling and a dwell of 5 h at 1500 °C. The green and the final densities of the samples were measured before and after dilatometry measurements from geometrical measurements. The push-rods and the reference sample consist of high purity alumina. A single crystal sapphire rod was used for calibration of the dilatometer.

X – ray photoelectron spectroscopy was performed on Pr-doped CeO<sub>2</sub> to determine the Pr<sup>3+</sup>/Pr<sup>4+</sup> ratio. Measurements were carried out in UHV (base pressures on the order of  $10^{-10}$  mbar, i.e.  $10^{-9}$  mbar with X-rays on), using a XR3 Twin Anode from Thermo Scientific as the X-ray source, with Al K $\alpha$  radiation. The anode power was set to 300 W, with a corresponding acceleration voltage and emission current of 15 kV and 20 mA. The analyzer is a PHOIBOS 100 Hemispherical Energy Analyzer from SPECS coupled to a HSA 3500 power supply. The measurements have been carried out in fixed analyzer transmission (FAT) mode with a pass energy of 50 eV. For both spectra, 4 scans were recorded, with an energy step of 0.3 eV. The XPS data were acquired by the SpecsLab software, while they were processed by the CasaXPS software.

Thermogravimetric analysis was carried out in a Netzsch 409 CD. Cylindrical, sintered and porous (CPF) pellets with a mass of 290 mg  $\pm$  10 mg were reduced under Ar 5.0 atmosphere ( $P_{0_2}$ ~3.5 × 10<sup>-4</sup> atm) at 1500 °C. Oxidation was started at 1000 °C in an atmosphere of 0.5 atm CO<sub>2</sub> (4.8) in Ar (5.0). Heating rates of 20 °C/min were employed for both heating and cooling and gas

flow rates were fixed to a total of 300 ml/min during oxidation and reduction. The samples were placed on a flat Pt-lid to avoid contamination from the alumina sample holder. A blank run with alumina and Pt-lid was subtracted from each measured sample.

### 3. Results & discussion

The sintering behavior of undoped and doped ceria produced by the solid state reaction was recorded using dilatometry. The green density of all samples is in the range of 56%–64% (Fig. 1(a)). Differences in green density of undoped and doped ceria are ascribed to differences in agglomerate size, in particle size and shape of the mixed metal oxide precursors (Table 1).

The temperatures of the onset of sintering and the peak sintering, for samples produced by the solid state reaction (SSR) synthesis, are presented in Fig. 1(b). For undoped CeO<sub>2</sub> the onset temperature is ~955 °C. No significant influence of HfO<sub>2</sub> or ZrO<sub>2</sub> dopant concentrations on the onset of sintering (±40 °C) could be observed, while it is increased considerably to ~1056 °C by doping with Pr<sub>6</sub>O<sub>11</sub>. In contrast, doping of CeO<sub>2</sub> with 5 mol - % TiO<sub>2</sub>, and doping of Hf<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2- $\delta$ </sub> with 2, 6 and 10 mol - % Li<sup>+</sup>, decreases the onset temperature to ~886 °C and ~870 °C respectively.

In undoped CeO<sub>2</sub>, the peak densification temperature is reached at ~1390 °C. In Zr and Hf doped CeO<sub>2</sub> this stage is stable within  $\pm 60$  °C, for the concentration range presented (0.05  $\leq x \leq 0.2$ ). Pr<sub>6</sub>O<sub>11</sub> doping increases the peak densification temperature to ~1500 °C, while 5 mol - % TiO<sub>2</sub> doped CeO<sub>2</sub> reaches the maximum densification rate below 1260 °C. At 10 mol - % TiO<sub>2</sub> doping the sample deforms in the given temperature range indicating mechanical instability. Higher TiO<sub>2</sub> concentrations (15, 20 mol - %)



**Fig. 1.** (a) Green densities, (b) onset of sintering and peak sintering temperature vs. dopant concentration for samples produced by SSR. Lines are guide to the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Polished and thermally etched (1500 °C, 30 min) cross sections of (a) CeO<sub>2</sub>, (b)  $Zr_{0.1}Ce_{0.9}O_{2-\delta}$ , (c)  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$ , (d)  $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ , (e)  $Li_{0.02}Hf_{0.09}Ce_{0.89}O_{2-\delta}$  and (f)  $Ti_{0.05}Ce_{0.95}O_{2-\delta}$  produced by SSR, and Pechini-synthesized (g) CeO<sub>2</sub>, (h)  $Zr_{0.1}Ce_{0.9}O_{2-\delta}$  and (i)  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$  after sintering for 5 h at 1600 °C.

lead to further softening and finally complete deformation of the samples. The latter becomes a technical challenge if the fabrication of a ceramic with microstructural stability at temperatures  $\geq$ 1500 °C is desired. Co-doping of Hf<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2- $\delta$ </sub> with Li<sup>+</sup> lowers the peak sintering temperature to ~1250 °C for Li<sup>+</sup> concentrations of 6 and 10 mol – %. For 2 mol – % Li doping the peak densification temperature was in the same range as for Hf<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2- $\delta$ </sub>. For both dopants, Ti<sup>4+</sup> and Li<sup>+</sup> the promotional effect on the sintering of ceria can be ascribed to a liquid phase sintering process induced by lowering the eutectic point of TiO<sub>2</sub>–CeO<sub>2</sub> and Li<sub>2</sub>O–CeO<sub>2</sub>, respectively [27,28].

Polished and thermally etched cross sections of undoped and doped CeO<sub>2</sub> synthesized by SSR and sintered for 5 h at 1600 °C are presented in Fig. 2. The SEM image of undoped CeO<sub>2</sub> features a grain size distribution of 59.0  $\mu$ m  $\pm$  2.9  $\mu$ m with intra- and intergranular porosity. According to Brook et al. [29,30] intragranular pores can be ascribed to pore-boundary separation due to differences in the pore and grain boundary velocity. The pore-boundary separation and thus the formation of intragranular pores can be affected by dopants which reduce the grain boundary velocity of CeO<sub>2</sub> [29,31].

Doping of CeO<sub>2</sub> with HfO<sub>2</sub> or ZrO<sub>2</sub> does not significantly affect the porosity (Fig. 2(a) and (b)). In principle, inter- and intragranular porosity remain for both dopants and the grain sizes decrease for both dopants over the investigated concentration range with a slight minimum at 15 mol-% doping concentration. A change in average grain size from 59.0  $\mu$ m  $\pm$  2.9  $\mu$ m in undoped ceria to 53.2–40.6  $\mu$ m in Zr doped CeO<sub>2</sub> and 53.9–35.6  $\mu$ m in Hf doped CeO<sub>2</sub> is apparent in the concentration range of 5–20 mol – % (see Fig. 3(a)).

Dense Pr doped ceria ceramics are formed after sintering for 5 h at 1600  $^{\circ}$ C, despite the observed retardation of sintering described earlier. Their microstructures show significantly decreased grain

sizes (Fig. 2(d)) with pores located mainly at grain boundaries. In comparison with pristine CeO<sub>2</sub> the grain sizes in Pr doped CeO<sub>2</sub> are decreased by a factor of 4, down to 14.7–10.2  $\mu$ m (Fig. 3(a)). Doping of CeO<sub>2</sub> with 5 and 10 mol – % Ti<sup>4+</sup> leads to a drastic increase of grain size to ~140  $\mu$ m. Moreover, the microstructures reveal the formation of secondary phases along the grain boundaries (Fig. 2(f)). Due to the lower contrast in BSE mode, we suggest that these secondary phases are Ti enriched deriving from a liquid-phase sintering process operating at these temperatures [32]. According to other studies a binary compound with CeTi<sub>2</sub>O<sub>6</sub> composition with a low melting point (T<sub>m</sub> ~ 1365 °C ± 5 °C) is formed [33],



Fig. 3. Average grain sizes of undoped and doped ceria produced by (a) SSR and (b) Pechini synthesis, after sintering for 5 h at 1600  $^\circ\text{C}.$ 

that enhances the mass transfer and leads to rapid grain growth and thus coarsening of the microstructure [34]. The co-doping of  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$  with Li<sup>+</sup> leads to a significant decrease in grain size from 42.7 µm in  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$  to 13.5 µm, 11.4 µm and 11.6 µm for 2-, 6- and 10 mol – % Li doping.

The trends in microstructural development and grain size evolution of CeO<sub>2</sub> and  $M_xCe_{1-x}O_{2-\delta}$  (M = Zr, Hf;  $0.05 \le x \le 0.2$ ) were compared to samples produced by a Pechini synthesis. In comparison with the SSR route, the Pechini synthesis yields microstructures with smaller grain sizes for the same sintering procedure (Fig. 3(b)). We ascribe that to the initially smaller particle size of the Pechini powders. However, the same trends compared to the SSR route hold true for Pechini-synthesized undoped and doped CeO<sub>2</sub>. Intra- and intergranular pores are present (Fig. 2) and the gain sizes decrease with increasing Hf and Zr dopant concentration. A local minimum in grain size exists for both dopants, with  $5.5 \pm 0.2 \,\mu$ m for  $5 \,\text{mol} - \% \,\text{Zr}^{4+}$  and  $8.3 \pm 0.3 \,\mu$ m for  $10 \,\text{mol} - \% \,\text{Hf}^{4+}$  compared to  $33.9 \pm 1.5 \,\mu$ m for pristine CeO<sub>2</sub> produced by Pechini synthesis (Fig. 3(b)).

Phase development after sintering was examined by recording XRD patterns of undoped and doped ceria produced by SSR synthesis, as presented in Fig. 4(a). All reflections can be assigned to the face-centered cubic (fcc) structure of CeO<sub>2</sub> and no secondary phases are detected in the XRD patterns of Zr, Hf, Pr and Li—Hf doped ceria. With increasing Zr and Hf concentrations the reflections shift to higher angles due to lattice contraction. This can be ascribed to the fact that solid solutions are formed where Ce<sup>4+</sup> is substituted by smaller Zr<sup>4+</sup> and Hf<sup>4+</sup>.

 $\Pr_x Ce_{1-x} O_{2-\delta}$  solid solutions were obtained by using a  $Pr_2^{III} Pr_4^{IV} O_{11}$  dopant (~33%  $Pr^{3+}$  (1.13 Å) and ~66%  $Pr^{4+}$  (0.96 Å)). After sintering the  $Pr^{3+}:Pr^{4+}$  ratio changed marginally to 28%  $Pr^{3+}$  and 72%  $Pr^{4+}$  as derived from XPS analysis. This  $Pr^{3+}:Pr^{4+}$  ratio was used for the determination of the theoretical lattice parameter according to Vegard's law (dotted lines Fig. 4(b)). The reflections of  $Pr_xCe_{1-x}O_{2-\delta}$  (0  $\leq x \leq 0.2$ ) shift to lower angles (Fig. 4(a)) with increasing x. We attribute this to the substitution of Ce^{4+} by the mixture of marginally smaller  $Pr^{4+}$  and larger  $Pr^{3+}$  cations. The codoping of  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$  with Li^+ (0.92 Å) does not lead to a significant shift of the reflections for 2, 6 and 10 mol-% doping (Fig. S2).

This indicates that Li is not substituting for  $Ce^{4+}$  in the grain structure. As suggested elsewhere we propose that Li is enriched in the grain boundaries [35].

A weak shift of reflections is apparent in the XRD patterns of  $TiO_2$  doped  $CeO_2$  and secondary phases are detectable in the  $2\theta$  range  $20-30^\circ$ . This goes in hand with the observations in SEM images (Fig. 2(f)), where secondary Ti-rich phases along the grain boundaries were detected.

Fig. 4(b) shows the lattice parameters, derived from Rietveld analysis, plotted vs. dopant concentration. The dotted lines indicate the theoretical lattice parameter according to Vegard's law for the different dopants [36]. For the samples produced by the Pechini synthesis (open symbols) the deviations from experimentally gained lattice parameters and Vegard's law are marginal. For the SSR synthesis (symbols) the deviations are only slightly larger compared to the Pechini synthesis (dotted lines) indicating that incorporation of the dopant oxides was almost complete. The Ti dopant does not obey Vegard's law, indicating that it is hardly incorporated into the fcc structure of ceria.

The phase development examined by XRD was validated using Raman spectroscopy. Raman spectra of pristine CeO<sub>2</sub> revealed only one peak at 465 cm<sup>-1</sup> (see supplementary information) which is assigned to O–Ce–O stretching in  $F_{2g}$  symmetry. With increasing Zr and Hf dopant concentration a shift to higher energies can be detected due to a decrease in lattice constant, *a*, and successive strengthening of the Ce–O and Zr–O/Hf–O bonds which is in excellent agreement with other work [37]. In Pr doped ceria a peak at 585 cm<sup>-1</sup> indicates distortion of the cubic ceria lattice by oxygen vacancies [38]. The same peak, but with lower intensity, can be detected for Hf and Zr doped ceria with increasing dopant concentration.

For redox cycling experiments porous samples of pristine, Zr, Hf, Pr and Li–Hf (co-) doped  $CeO_2$  were produced as shown in Fig. 5(a)–(f). For this purpose carbon pore forming particles were added to the mixed metal oxides in a 1:1 volume-ratio prior to sintering.

The volume of interconnected porosity was examined by infiltrating the porous samples with an organic resin. After grinding and polishing of the embedded samples, SEM images were



**Fig. 4.** (a) XRD patterns of CeO<sub>2</sub> and SSR – synthesized  $M_xCe_{1-x}O_{2-\delta}$  (0.05  $\leq x \leq 0.2$ ) and (b) lattice parameters *a* vs. dopant concentration *x* in  $M_xCe_{1-x}O_{2-\delta}$  synthesized by SSR (closed symbols) and Pechini (open symbols). Theoretical lattice parameters of doped ceria are shown as dotted lines. Only two data points for Ti doped ceria are presented due to softening of 15 mol – % and 20 mol – % Ti doped CeO<sub>2</sub>.



**Fig. 5.** Cross sections of porous, SSR synthesized (a) CeO<sub>2</sub>, (b) Zr<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub>, (c) Hf<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub>, (d) Pr<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub>, (e) Li<sub>0.06</sub>Hf<sub>0.094</sub>Ce<sub>0.846</sub>O<sub>2-δ</sub> and (f) Ti<sub>0.05</sub>Ce<sub>0.95</sub>O<sub>2-δ</sub> produced by adding 50vol-% CPF prior to sintering for 5 h at 1600 °C. (g) Interconnected porosity, e<sub>2D</sub>, of undoped and doped ceria produced by SSR plotted vs. dopant concentration. (h) SEM image of a polished cut through a polymer-infiltrated ceramic where filled (interconnected) and unfilled pores can be distinguished.

![](_page_6_Figure_1.jpeg)

**Fig. 6.** 1st (left row) and 2nd (right row) RedOx cycle of  $Zr_xCe_{1-x}O_{2-\delta}(a)$ , (b),  $Hf_xCe_{1-x}O_{2-\delta}(c)$ , (d) and  $Li_x(Hf_{0.1}Ce_{0.9})_{1-x}O_{2-\delta}(e)$ , (f). Pristine  $CeO_{2-\delta}$  is plotted as reference in (a)–(d) in black. All mass changes are normalized with respect to the point at which  $Ar/CO_2$  is introduced into the TG.

recorded using a BSE detector. In the resulting micrographs interconnected and thus resin-infiltrated pores have a lower contrast than the ceramic matrix as exemplarily demonstrated in Fig. 5(h). Accordingly, the interconnected porosity,  $\varepsilon_{2D}$ , can be derived from the area of infiltrated pores divided by the control area, assuming an isotropic pore network.

Fig. 5(g) shows the plot of interconnected (resin-infiltrated)

porosity,  $\varepsilon_{2D}$ , vs dopant concentration of samples produced by SSR

after sintering for 5 h at 1600 °C. The added amount of CPF prior to sintering corresponds to a theoretical  $\varepsilon_{2D, Start} = 0.5$  (50%), which is indicated by the dotted line in Fig. 5(g).

In pristine CeO<sub>2</sub> a 2D-porosity of 40.5% is measured which corresponds to a closure of 9.5% interconnected porosity during sintering. Doping of ceria with Pr, Zr and Hf reduces the open porosity to 26–39%. While in Zr doped CeO<sub>2</sub> the 2D porosity varies in a smaller range of 39.4-35.8%, close to the value of pristine CeO<sub>2</sub>

(40.5%), a decrease of  $\varepsilon_{2D}$  in Hf<sub>x</sub>Ce<sub>1-x</sub>O<sub>2- $\delta$ </sub> from 35.9% (x = 0.05) to 26.3% (x = 0.2) is observed. Similar trends are found in Pr doped CeO<sub>2</sub> where  $\varepsilon_{2D}$  is in the range of 35.0%–27.8%.

For Ti doped CeO<sub>2</sub> complete closure of interconnected porosity is observed. The sintering properties and microstructure (Figs. 1 and 2) suggested the formation of a large ratio of liquid phase already at temperatures <1400 °C. Therefore, the densification rates are drastically increased due to enhanced mass transport by the liquid phase and pores are annihilated [39,40].

In Li–Hf co-doped CeO<sub>2</sub> the 2D porosity is between 40.0% (2 mol-% Li) and 43.0% (10 mol-% Li) indicating that  $(\text{Li},\text{Hf})_x\text{Ce}_{1-x}\text{O}_{2-\delta}$  retains open porosity to a much higher extent than  $\text{Hf}_{0.1}\text{Ce}_{1-x}\text{O}_{2-\delta}$  ( $\epsilon_{2D} = 32\%$ ).

In ceria based ceramics, grain coarsening is mainly driven by cation diffusion through the grain boundaries under the present conditions [41]. Accordingly, we suggest that Hf and Pr doping increase the cation mobility across the grain boundaries of ceria. Zr doping has no significant effect, while Li co-doping reduces the cation mobility at high temperatures. It is unclear whether the inhibited grain coarsening derives from a change of the grain boundary structure or the formation of a glassy Li–Ce–O layer in which the bulk has a low solubility. Therefore, further studies have to be employed to obtain evidence on the function of Li in co-doped ceria.

Fig. 6 shows two successive redox cycles of CeO<sub>2</sub> and  $Zr_xCe_{1-x}O_{2-\delta}$  ( $0 \le x \le 0.2$ ) as determined by thermogravimetric analysis. During heating to, and the isotherm at 1500 °C under Ar, a mass loss of the sample is observed, which is correlated to the release of O<sub>2</sub> according to Eq. (1). The sample is then cooled down to 1000 °C, where CO<sub>2</sub> splitting is initiated by introducing an Ar/CO<sub>2</sub> mixture (0.5 atm CO<sub>2</sub>). A rapid mass increase is measured which can be attributed to CO<sub>2</sub> splitting and the successive oxygen uptake of CeO<sub>2- $\delta$ </sub>, both resulting in the formation of carbon monoxide according to Eq. (2).

From the mass loss/mass gain, indicated as  $\Delta m_{red}/\Delta m_{ox}$  for pristine CeO<sub>2</sub> in Fig. 6(a), the amount of O<sub>2</sub> and CO produced can be calculated according to:

$$[O_2] = \frac{\Delta m_{red}}{M_{O_2}} \tag{4}$$

$$[CO] = \frac{\Delta m_{ox}}{M_0} \tag{5}$$

where  $\Delta m_{red}$  and  $\Delta m_{ox}$  are the mass loss during reduction and oxidation respectively. Subsequently, the reduction yield,  $X_{red}$ , of  $M_xCe_{1-x}O_{2-\delta}$ , corresponding to the fraction of  $Ce^{3+}$  over the total concentration of Ce cations, can be calculated according to:

$$X_{red} = 4 \cdot \Delta m_{red} \frac{M_{MO_2}}{(1-x)M_{O_2}} \tag{6}$$

where *x* is the dopant concentration and  $M_{MO_2}$  is the molar mass of the mixed metal oxide,  $M_{O_2}$  is the molar mass of  $O_2$  and  $M_0$  is the molar mass of atomic oxygen. For a better comparison of the oxidation kinetics of the following samples, the mass changes in Fig. 6 are normalized with respect to the point at which Ar/CO<sub>2</sub> is introduced into the TG.

In pristine ceria the reduction starts at ~1060 °C as indicated by the onset of mass loss (Fig. 6 (a)). After an isotherm of 100 min at 1500 °C the mass loss of CeO<sub>2</sub> is ~0.40%. During successive cooling to 1000 °C in an Ar atmosphere a mass increase is observed owing to oxidation reactions with residual O<sub>2</sub> in the TG system [17]. When oxidation with CO<sub>2</sub> is initiated at 1000 °C, pristine CeO<sub>2</sub> reaches 90% of its initial oxidation state (0.36% mass gain) after 2 min which is in agreement with thermodynamic [42] and kinetic [8,43] data on pristine CeO<sub>2</sub>. Oxidation proceeds to completion after a total of 9 min. During the 2nd redox cycle the mass loss during reduction is 0.4%, while the mass gain during successive oxidation is only 0.37% indicating a marginally incomplete oxidation.

For  $Zr_xCe_{1-x}O_{2-\delta}$  the mass losses during the 1st cycle are 0.45%, 0.54% and 0.78% for x = 0.05, 0.1 and 0.2 respectively (Fig. 6(a)). During the 2nd cycle (Fig. 6(b)) these values decrease slightly to 0.42% and 0.51% for x = 0.05 and 0.1. Moreover, the onset temperature of reduction decreases proportionally with increasing Zr concentration down to ~950 °C in  $Zr_{0.2}Ce_{0.8}O_{2-\delta}$ . With increasing Zr concentrations the oxidation reaction slows down significantly. Reaching the oxidation state of ceria (0.36% mass gain) for  $Zr_xCe_{1-x}O_{2-\delta}$  requires 5 min, 11 min and 10 min for x = 0.05, 0.1 and 0.2, respectively in the first cycle. However, to reach 90% of their (individual) initial oxidation state requires 10 min, 44 min and 125 min for x = 0.05, 0.1 and 0.2 respectively, in the first cycle. The oxidation rates during the 2nd cycle do not change compared to the 1st cycle. Compared to the mass loss during reduction, the oxidation proceeds stoichiometrically for x = 0.05 and 0.1. For x = 0.2 the initial oxidation state is not reached within 180 min of oxidation.

Solid solutions of  $Hf_xCe_{1-x}O_{2-\delta}$  show a similar trend as  $Zr_xCe_{1-x}O_{2-\delta}$ . The mass losses during the 1st redox cycle are 0.55%, 0.63%, 0.65% and 0.75% for x = 0.05, 0.1, 0.15 and 0.2 respectively (Fig. 6(c)). During the 2nd cycle the mass losses are similar (0.55%, 0.63%, 0.65% and 0.72%, Fig. 6(d)). The onset of reduction decreases proportionally with increasing Hf concentration to ~930 °C in  $Hf_{0.2}Ce_{0.8}O_{2-\delta}$ , while the time required for full oxidation increases. Reaching the oxidation state of ceria (0.36% mass gain) requires 7 min, 14 min, 34 min and 50 min for x = 0.05, 0.1, 0.15 and 0.2, respectively in the first oxidation step. The reduction and oxidation reaction proceed stoichiometrically for 5 mol – % Hf doping. For higher Hf concentrations (>10 mol – %) the initial oxidation state is not fully recovered, which has also been observed in other studies on the same material [44].

The addition of Li to  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$  leads to very similar mass losses (evolution of  $O_2$ ) as compared to  $Hf_{0.1}Ce_{0.9}O_{2-\delta}$  during the 1st reduction step. The mass losses in  $Li_x(Hf_{0.1}Ce_{0.9})_{1-x}O_{2-\delta}$  are 0.63%, 0.56%, 0.55% and 0.53% for x = 0, 0.02, 0.06 and 0.1 respectively (Fig. 6(e)). The onset of mass loss (reduction) does not change upon additional Li doping. During successive oxidation (uptake of  $O_2$ ) the mass gains are 0.5%, 0.56%, 0.56% and 0.53% for the same

![](_page_7_Figure_17.jpeg)

Fig. 7. Two successive Redox cycles of  $Pr_xCe_{1-x}O_{2-\delta}$ .

![](_page_8_Figure_1.jpeg)

**Fig. 8.** (a)  $O_2$  release rates, (b) CO generation rates, (c) reduction yield and (d)  $CO/O_2$  ratio of  $M_xCe_{1-x}O_{2-\delta}$  (M = Zr, Hf, (Li,Hf);  $0 \le x \le 0.2$ ) averaged over two successive cycles. For  $Zr_{0.2}Ce_{0.8}O_{2-\delta}$  data is taken from the first redox cycle only.

compositions. During the second reduction step, the mass losses (evolution of O<sub>2</sub>) are 0.53%, 0.55%, 0.5% and 0.51% for x = 0, 0.02, 0.06 and 0.1 (Fig. 6(f)). Full oxidation (mass gain) is observed for all samples in the 2nd redox cycle.

The mass losses of CeO<sub>2- $\delta$ </sub> and Pr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2- $\delta$ </sub> (x = 0.05, 0.1) are presented in Fig. 7. In Pr doped ceria reduction starts below 700 °C (Fig. 7). A first plateau is reached at around 1040 °C, indicated by dotted lines labeled  $\Delta m_{1, x} = 0.05/0.1$ , after which the reduction again accelerates in a similar fashion to pristine CeO<sub>2</sub>. Therefore, we divide the total mass loss of Pr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2- $\delta$ </sub> into two individual steps  $\Delta m_1$  and  $\Delta m_2$  (Fig. 7). The mass loss  $\Delta m_1$  increases with increasing Pr concentration, with 0%, 0.14% and 0.38% in 0-, 5- and 10 mol - % Pr doped CeO<sub>2</sub>, respectively. According to Adachi and Imanaka two different reduction steps are involved. Firstly, below 750 °C the reduction of Pr<sup>4+</sup> according to:

$$\left(Pr_{y}^{IV}Pr_{1-y}^{III}\right)_{x}Ce_{1-x}^{IV}O_{2-\delta} \rightarrow \left(Pr_{z}^{IV}Pr_{1-z}^{III}\right)_{x}Ce_{1-x}^{IV}O_{2-\delta}$$
(7)

where *y* and *z* reflect the  $Pr^{4+}:Pr^{3+}$  ratio before and after reduction respectively. After the first mass loss  $(\Delta m_1)$ , *y* exceeds *z* [45]. In other words, the mass loss  $\Delta m_1$  is equal to the complete reduction of remaining  $Pr^{4+}$  to  $Pr^{3+}$ .

After cooling to 1000 °C the samples are exposed to 0.5 atm CO<sub>2</sub> leading to oxidation as indicated by a mass increase (Fig. 7). While undoped ceria oxidizes rapidly, a lower oxidation rate is observed for  $Pr_xCe_{1-x}O_{2-\delta}$ . Moreover, the total mass gain at thermodynamic equilibrium (steady state) is only equal to the respective mass loss  $\Delta m_2$  for both, x = 0.05, 0.1 indicating that  $Pr^{3+}$  could not be reoxidized to  $Pr^{4+}$  under present conditions. Therefore, praseodymia proves ineffective in increasing the redox performance of CeO<sub>2</sub>.

Table 2
$O_2$ release, reduction yields and fuel (CO) release of $M_x Ce_{1-x} O_{2-\delta}$ derived from TG analysis

Material	First cycle			Second cycle		
	$O_2$ released (µmol/g)	Reduction yield (%)	CO generated (µmol/g)	$O_2$ released (µmol/g)	Reduction yield (%)	CO generated (µmol/g)
CeO <sub>2</sub>	128	8.83	256	125	8.61	231
Zr <sub>0.05</sub> Ce <sub>0.95</sub> O <sub>2</sub>	137	9.76	275	25	8.49	269
Zr <sub>0.1</sub> Ce <sub>0.9</sub> O <sub>2</sub>	169	12.55	331	159	11.86	325
Zr <sub>0.2</sub> Ce <sub>0.8</sub> O <sub>2</sub>	244	19.80	474	-	-	_
Hf <sub>0.05</sub> Ce <sub>0.95</sub> O <sub>2</sub>	139	10.22	294	131	9.62	288
$Hf_{0.1}Ce_{0.9}O_2$	197	15.45	312	167	13.08	331
Hf <sub>0.15</sub> Ce <sub>0.85</sub> O <sub>2</sub>	204	17.08	377	187	15.69	353
$Hf_{0.2}Ce_{0.8}O_2$	235	21.17	353	223	20.11	419
$Li_{0.02}Hf_{0.098}Ce_{0.882}O_{2-\delta}$	178	14.07	350	170	13.50	333
$Li_{0.06}Hf_{0.094}Ce_{0.846}O_{2-\delta}$	172	14.01	344	156	12.71	313
$Li_{0.1}Hf_{0.09}Ce_{0.81}O_{2-\delta}$	166	13.88	338	159	13.33	306

In pristine CeO<sub>2</sub> under present conditions, an average oxygen release of ~127  $\mu$ mol/g (calculated from Eq. (4)) is gained during both redox cycles (shown Fig. 8(a) and printed in Table 2). This corresponds to a fraction of 8.5% Ce<sup>3+</sup> cations (calculated from Eq. (6)) formed during reduction (Fig. 8(c)). The CO generation equals and average of ~244  $\mu$ mol/g (Fig. 8(b)). The overall CO/O<sub>2</sub> – ratio is 1.93 (Fig. 8(d)) owing to a slightly nonstoichiometric reduction and oxidation reaction during the 2nd redox cycle.

The O<sub>2</sub> release is increased proportionally with increasing Zr and Hf concentration (Table 2). In both cases this reflects a larger fraction of formed Ce<sup>3+</sup> cations, as compared to pristine ceria (Fig. 8(c)). The fraction of formed Ce<sup>3+</sup> is more than doubled at 20 mol-% doping to 19.8% (Zr) and 20.6% (Hf). This can be attributed to a higher driving force for the formation of 7-fold coordinated metal sites which has been explained earlier. The CO generation yields also increase proportionally with increasing Hf and Zr concentration. Oxidation proceeds stoichiometrically in Zr doped ceria as expressed by CO/O<sub>2</sub> ratios between 1.94 and 2 (Fig. 8(d)). In comparison, the CO/O<sub>2</sub> ratios of Hf doped ceria ( $\geq$ 10 mol-%) are successively lower (<1.9). In other words; Hf doped ceria reduces to a higher extent than Zr doped ceria per gramm but due to incomplete oxidation the CO production rates are lower.

For both dopants the oxidation reaction slows down significantly. Considering the similarities in porosity of CeO<sub>2</sub> and  $Zr_xCe_{1-x}O_{2-\delta}$  the kinetics are mainly driven by the amount of dopant. This indicates that lattice distortions induced by the smaller  $Zr^{4+}$  (and  $Hf^{4+}$ ) cation stabilize the reduced state of doped ceria.

The reduction yields of  $\text{Li}_x(\text{Hf}_{0.1}\text{Ce}_{0.9})_{1-x}O_{2-\delta}$  do not change with increasing Li concentration indicating that Li does not improve the achievable nonstoichiometry. The same holds true for the reaction kinetics. The CO generation yields are slightly higher in Li co-doped, compared to Hf doped ceria with the highest CO generation at 2 mol-% Li doping (333 µmol/g) as shown in Fig. 8(b). The CO/O<sub>2</sub> ratios of all Li doped samples are successively higher than 1.97. This demonstrates that Li has a promotional effect on the thermodynamics of the oxidation reaction and may be a promising co-dopant for other ceria based redox ceramics.

#### 4. Conclusions

Ceria based oxygen storage materials were synthesized using two different synthesis routes: Firstly, a state-of-the-art solid state reaction synthesis using a µm-sized ceria precursors and secondly, a Pechini synthesis. Doping of CeO<sub>2</sub> with ZrO<sub>2</sub>, HfO<sub>2</sub> and Pr<sub>6</sub>O<sub>11</sub> leads to the incorporation of Zr<sup>4+</sup>, Hf<sup>4+</sup> and Pr<sup>3+</sup>/Pr<sup>4+</sup> into the ceria lattice to almost the same extent for both, solid state reaction and Pechini synthesis.

By adding carbon pore forming particles prior to sintering,

porous ceramics are obtained, that allow for high mass transport through an interconnected pore network during thermochemical redox cycles. Sintering for 5 h at 1600 °C induces pore annihilation that is severe for Ti-, and highly pronounced for Hf- (and Pr-) doped ceria. Pristine, Zr doped and Li—Hf co-doped ceria effectively retain open porosity.

The phase pure fcc – structured  $M_xCe_{1-x}O_{2-\delta}$  (M = Zr, Hf, Pr) solid solutions show excellent CO<sub>2</sub> splitting performance according to TG analysis. The fuel (CO) production rates are increased linearly with increasing Hf and Zr dopant concentration up to 20 mol-% doping. Upon co-doping over a wide range of Li-concentrations (2–10 mol-%), the oxidation reaction can be promoted leading to highly stoichiometric reduction—oxidation reactions.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.09.073.

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