

Electronic Supporting Information

Accelerated ceria-zirconia solubilization by cationic diffusion inversion under low oxygen activity

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Experimental

Controlled thermal-chemical treatment-reoxidation route

Composite samples were treated as schematically illustrated in Fig. S1. The thermochemical treatments consist in a sequence of steps including:

- In flowing 9 % H₂-N₂, heating, at constant rate of 1 °C min⁻¹, from 400 to 1400 °C (i.e. sintering temperature, T_{sint}), a holding time of 1 hour and cooling to 900 °C at constant rate of 1 °C min⁻¹. This was followed by a change in the inlet gas composition from 9% H₂-N₂ to pure N₂.
- In N₂, treated at constant temperature of 900 °C for 5 hours and then changing gas composition to air.
- In air, hold for 5 hours at 900 °C followed by cooling to room temperature at constant cooling rate (1 °C min⁻¹).

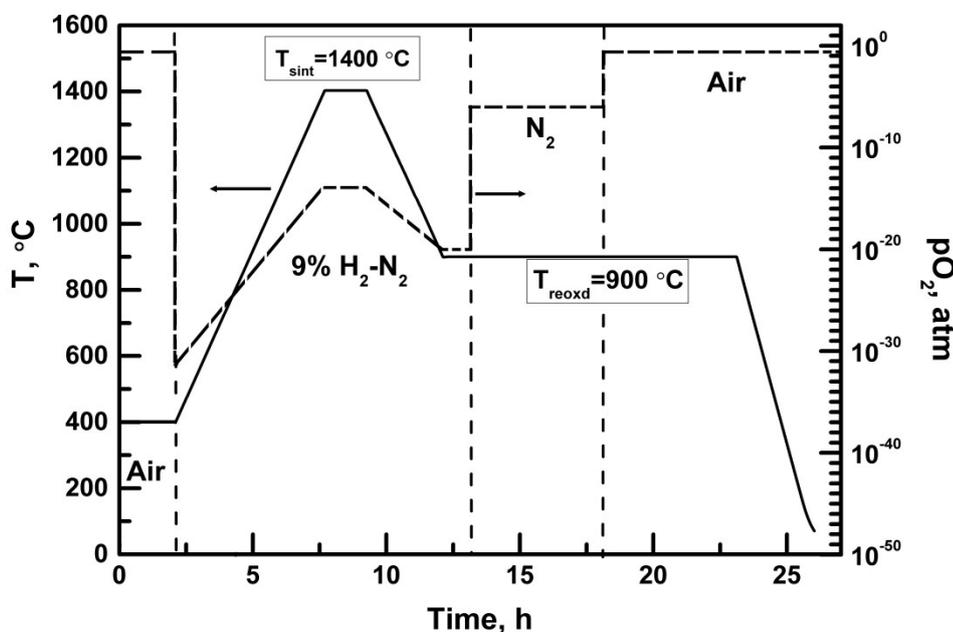


Fig. S1 Re-oxidation profile for dilatometry experiments. Sintering was performed at T_{sint} = 1400 °C in reducing atmosphere (9% H₂-N₂), then the temperature was reduced to T_{reoxd} = 900 °C for reoxidation and cooling in air.

Fig. S1 also shows the expected pO_2 profile expected at the different steps of the heat treatment as a result of the gas mixture and the temperature profile. Particularly, in 9% H_2-N_2 , pO_2 ranged from *ca.* 10^{-32} atm (at 400 °C) to 10^{-14} atm at 1400 °C to *ca.* 10^{-20} atm at 900 °C (see also Fig. S2). In N_2 and in air, the expected pO_2 is constant at *ca.* 10^{-6} atm and 0.21 atm, respectively. As also described in our previous work, this methodology allows oxidizing the materials, avoiding mechanical shocks, usually associated to the chemical expansion-contraction process in the elastic regime at low temperatures that can result in crack formation and mechanical failure of specimens.¹

Results and discussion

CGO vacancy concentration

Fig. S2 shows the expected oxygen defect concentration in CGO as function of temperature. This was calculated according to thermodynamical values reported by Wang *et al.* and recalculated for the reactive mixture 9 vol. % H_2 in inert N_2 .¹⁻⁵ The plot also shows the calculated pO_2 as a function of the thermal treatment changing as a result of the hydrogen mixtures oxidation. The plot shows increasing concentration of the c-type phase Ce_2O_3 in solid solution for temperatures above 1000 °C. Calculations for pure CeO_2 decomposition into c-type phase are reported in 1, while details on calculations and experimental results on CGO and YSZ are also reported in previous works.²⁻⁴

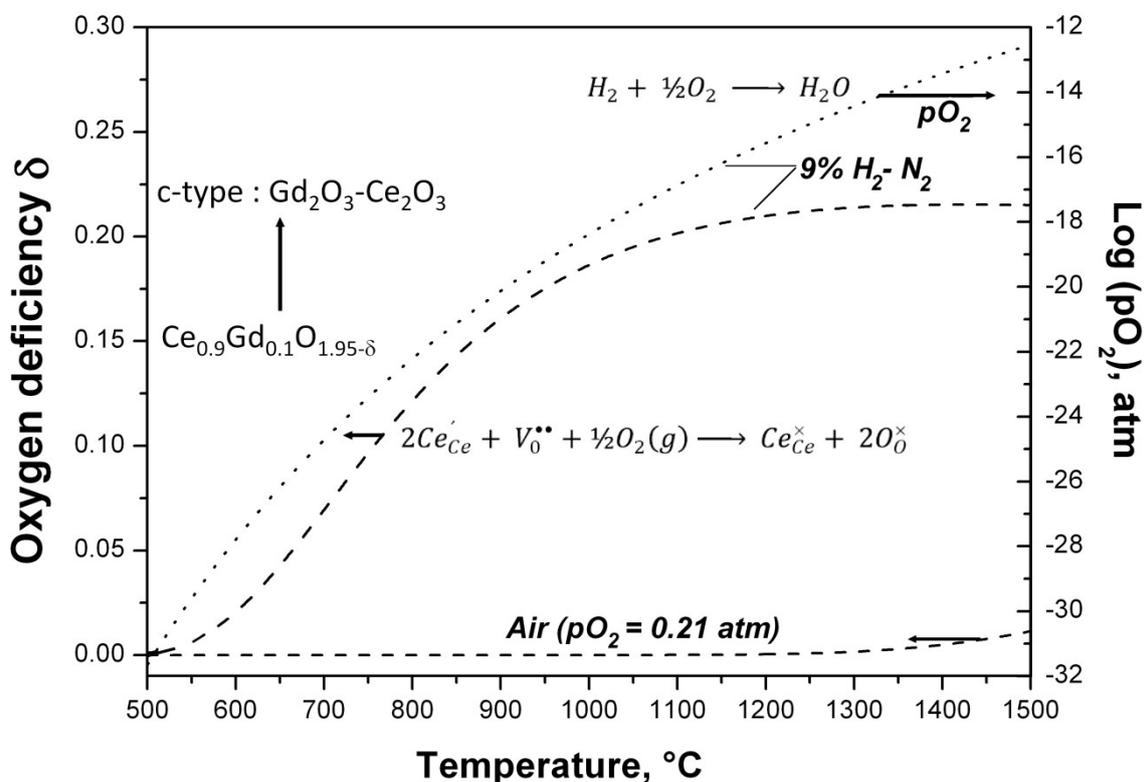


Fig. S2- Oxygen deficiency d in $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ as a function of temperature, calculated as in refs. 1 and 2 (equilibrium conditions) in air and 9% H_2-N_2 . Dotted line shows the calculated oxygen partial pressure (Y2 axis) of H_2/O_2 equilibrium at different temperatures for the 9% H_2-N_2 mixture.

CGO chemical and thermal expansion

Fig. S3 shows the temperature dependence of both chemical and thermal expansion calculated for pure ceria due to the chemical reduction Ce^{4+} to Ce^{3+} . The curves are plotted on the basis of thermodynamical values, *i.e.* at the equilibrium state, as result of chemical reduction in 9 vol. % H_2-N_2 .^{1,2} The plot emphasizes the change in volume expected in the treatment shown in Fig. S1 and schematized in Fig. 5.

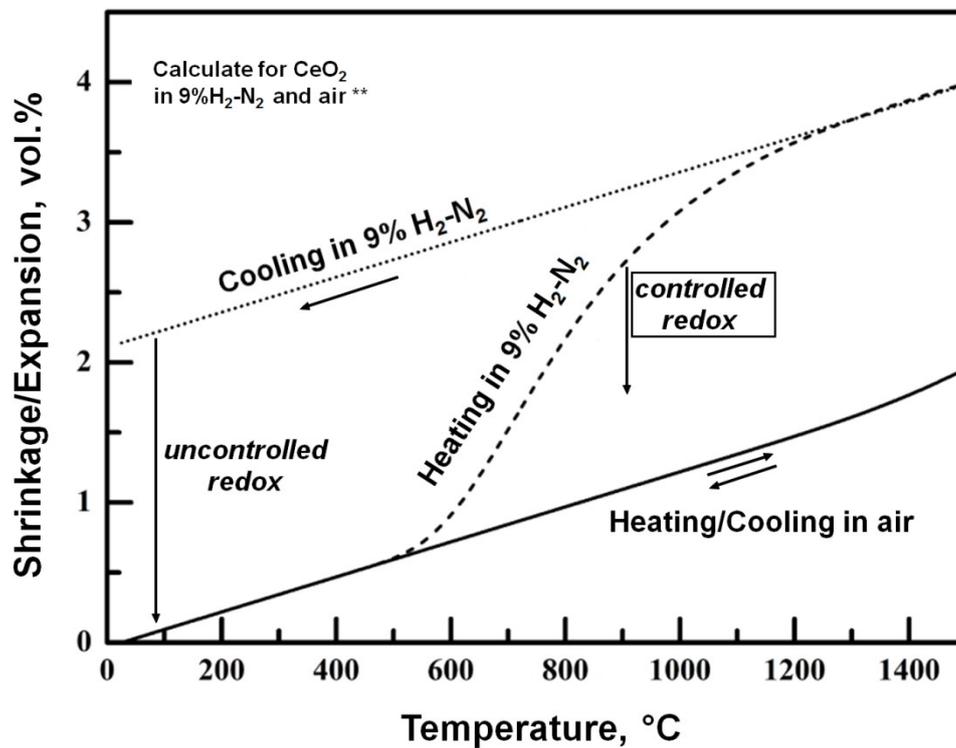


Fig. S3- Calculated shrinkage/expansion due to chemical and thermal treatment for heat-treatment of CGO in 9% H₂-N₂ and in air as a function of temperature.

References

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