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Effect of chemical redox on Gd-doped ceria mass diffusion

D. W. Ni[a], D. Z. de Florio[b], D. Marani[a], A. Kaiser[a], V. B. Tinti[b], and V. Esposito[a †]

Valence and size of cations influence mass diffusion and oxygen defects in ceria. Here we show that Ce^{4+} to Ce^{3+} reduction, at high temperatures and low oxygen activity, activates fast diffusion mechanisms which depend on the aliovalent cations concentration. As a result, polycrystalline solid solutions with enhanced electrochemical properties are formed.

Ceria based compounds are used in a broad range of technologies such as catalysis, environmental, electromechanical, electrochemical, and various emerging energy technologies. [1-5] Such an extensive use of this materials is due to the unique combination of different properties such as high ionic conductivity, mixed electronic and ionic conductivity, large oxygen storage and exchange capabilities, which are all linked to the ability of the material to undergo rapid Ce^{3+}/Ce^{4+} redox cycles and form oxygen vacancies. [1-5] Moreover, ceria solid solutions usually show exceptionally high chemical stability, even in extremely harsh and corrosive environments, in the presence of sulphur or at very high operative temperatures. [3, 5-8]

Although ceria compounds are usually considered very stable refractory materials with low mass diffusion and reactivity, there are some important exceptions. In previous works, we showed that $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ can actually undergo fast mass diffusion at low oxygen partial pressure ($pO_2 < 10^{-12}$ atm) above 800 °C. Fast mass diffusion leads to significant microstructural transformations, low viscosity and even to low temperature solid state reaction with alumina. [9-12]

A mechanistic explanation of these phenomena can be given on the basis of the peculiar defect chemistry of ceria. [9, 11] At high oxygen activity (*e.g.* in air), mass diffusion in ceria is generally severely inhibited. Presence in the $Ce(IV)O_2$ solid solution of aliovalent cations with lower charge and larger ionic dimensions, such as of Gd^{+3} and Ce^{3+} itself (*i.e.* $Gd^{3+} \approx 1.053$ Å and $Ce^{3+} \approx 1.01$ Å *vs* $Ce^{4+} = 0.907$ Å ionic radii in the CeO_2 8-fold cubic coordination), originates coulombic and steric "trapping" effects of the Ce^{+4} cation diffusion.

[13] The mass diffusion is influenced by dopants concentration which is especially limited at the grain boundary, where aliovalent cations are usually segregated. In sintering science, such trapping effect due to *alio*-dopant (and impurities) at the grain boundary is known as *solute drag effect*, *i.e.* the mass diffusion is controlled by the diffusion of the dopant solute. [13, 14]

Particularly in reducing conditions (*i.e.* low oxygen activity), CeO_2 solid solution is reduced $CeO_{2-\delta}$ with loss of O_2 (gas), oxygen defects ($V_O^{\cdot\cdot}$) formation and Ce^{4+} reduction to Ce^{3+}. The Ce^{3+} and Gd^{3+} have the same valence and similar cation sizes (Ce^{3+} ionic radius 1.01 Å and Gd^{3+} 1.053 Å, also in the $CeO_{2-\delta}$ with 6-fold octahedral coordination). In such conditions, the solute drag effect due to the Gd^{+3} is drastically reduced, and consequently, the mass diffusion is unleashed. [9, 11]

A more detailed understanding of the effects of mass diffusion mechanisms in doped ceria is of large importance because it opens new opportunities for using these materials in emerging technologies or improving existing applications. Particularly, in this study we investigate the impact of aliovalent dopant concentration on highly defective doped ceria mass diffusion, both in reducing and oxidizing conditions. The concentration of the dopant can influence both the electrochemical and the microstructural features, when treated in air. [13] Here we explore the reciprocal influence of the chemical reduction and dopant concentration on measurable mass diffusion effects, such as densification and grain growth (*i.e.* sintering), and their influence on the final ionic conductivity (*i.e.* oxygen defect transport).

For this analysis nanometric powders of 10-20 nm (TEM, JEOL, Japan) of Gd-doped ceria solid solutions (*i.e.* $Ce_{1-x}Gd_xO_{2-d}$, x=0, 0.01, 0.10 and 0.30; referred hereafter as CeO_2, CGO0.1, CGO10 and CGO30, respectively) were synthesized by Pechini method and used as starting materials. [15] Pellets with 6 mm in diameter and ~ 4 mm in thickness were obtained by uniaxial pressing, which have relative green densities of ~ 48%. Dilatometry of the pellets was performed by thermo-mechanical analysis (TMA 402 F1 Hyperion, Netzsch, Germany). The samples were fired to 1400 °C at a heating rate of 3 °C min^{-1} and held for 4h, either in air or reducing atmosphere (9%H_2-N_2, $10^{-31} < pO_2 < 10^{-12}$ atm, depending on temperature [9]).The samples sintered in reducing conditions were re-oxidized at 1100 °C

[a] *Department of Energy Conversion and Storage, Technical University of Denmark (Risø Campus), DK-4000 Roskilde, Denmark.*
[b] *Universidade Federal do ABC, 09210-580 - Santo André - SP - Brazil.*
[c] *† Corresponding author: vies@dtu.dk(V. Esposito), +45 46775637*

as reported in ref. [11]. This latter treatment is crucial to preserve the mechanical integrity of the material and avoid chemo-mechanical shock which can destroy the samples. It is also important to remark that the final treatment in air at 1100 °C ensures a rapid oxidation of the cerium cations, decreasing thus the concentration of both the electronic (i.e. Ce^{3+}) and the oxygen defects ($V_O^{\cdot\cdot}$) to the thermodynamical equilibrium values. [11]
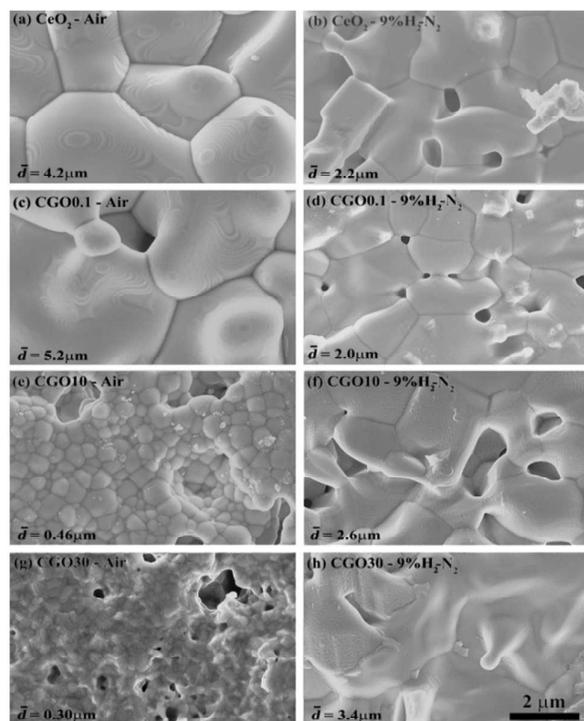
Fig. 1 shows the impact of aliovalent dopant concentration (i.e. Gd in 0, 0.1, 10 and 30 mol%), together with the influence of atmospheric conditions (reducing and oxidative atmospheres), on diffusion. This is represented as shrinkage (left) and shrinkage rate (right) plots due to densification of CeO_2, CGO0.1, CGO10 and CGO30 compacts measured both in air and 9% H_2-N_2 at the TMA. The densification of the samples, measured as linear shrinkage activated by the mass diffusion, starts at temperatures as low as ~600 °C in 9% H_2-N_2 for all the investigated materials. This is around 100−200 °C lower than those sintered in air. Despite a lower onset temperature for the linear shrinkage occurring in reducing condition, the final shrinkage is dependent on dopant concentration. With no dopant or low dopant concentration (CeO_2 and CGO0.1), the final shrinkage is higher in air, which indicates that the densification of CeO_2 and CGO0.1 is inhibited under reducing conditions. On the other hand, it is also observed that sintering is enhanced with low dopant content (i.e. CGO0.1), both in air and reducing conditions. At high dopant concentrations (CGO10 and CGO30), the final shrinkage is comparable under reducing and oxidative atmosphere, despite the mass diffusion is fully activated at lower temperature in 9%H_2-N_2. The TMA also indicated that the densification proceeded in a multi-stage way without the typical plateau of the final stage of the sintering. The shrinkage rate plots represent how the mass diffusion activity changes with the temperature. [9, 11, 14] **Fig.1** on the right shows and confirms that the
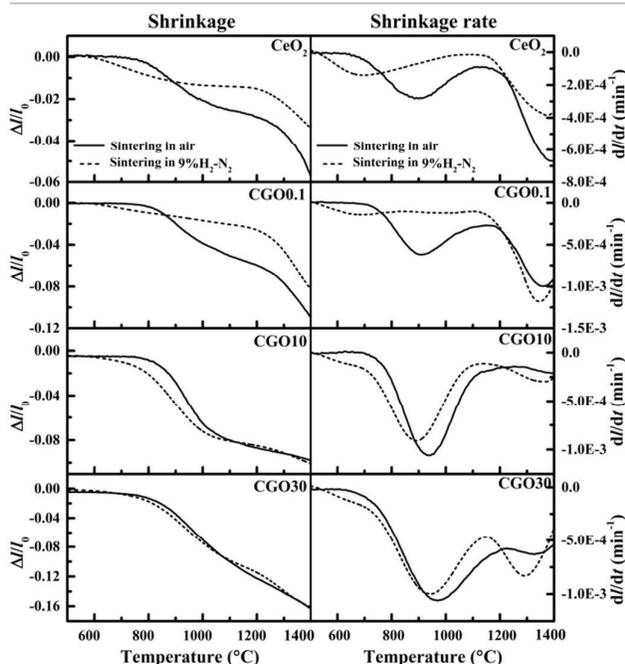
sintering activity strongly depends on the temperature, exhibiting more than one stage for all the samples and conditions. Particularly, the presence of shrinkage activity at high temperatures above 1200 °C, suggests that the residual porosity in the sample was not homogeneous in the compacts and densification require higher temperatures. Such a heterogeneous densification process is typical of nanometric powders and it was previously observed in gadolinium doped ceria as results of agglomeration, which is almost inevitable in nano-powders dry processing. [16-18] As result of such limitations, the final density of the samples at 1400 °C were comparable for each composition.

Despite the differences observed in the densification process at the TMA, the scanning electron microscopy (FESEM, Supra, Carl Zeiss, Germany), conducted to investigate grain growth in the doped ceria compacts, clearly reveals mass diffusion effect in the grain growth after the thermal treatments. **Fig. 2** shows the microstructural features of the CeO_2, CGO0.1, CGO10 and CGO30 compacts treated in air and 9% H_2-N_2 at 1400 °C for 4h. After the treatment, all the samples have microstructures with typical polycrystalline arrangement which are strongly dependent on dopant concentration and sintering atmosphere. Particularly, samples with no dopant or low dopant concentration, i.e. CeO_2 and CGO0.1, showed average grain sizes of ~4.2 μm and 5.2 μm, respectively, when sintered in air. The grain size was ~2.2 μm and 2.0 μm, respectively, when the same materials are sintered in reducing atmosphere. Grain size statistics was determined by micrograph elaboration methods, as reported in refs [14]. These results confirm the TMA data (**Fig.1**) that mass diffusion can be enhanced at low dopant concentration (i.e. CGO0.1). It also confirms that mass diffusion in CeO_2 and CGO0.1 is inhibited under reducing condition (i.e. 9% H_2-N_2). As also reported by Chen et al., this effect is likely due to the self-induced solute drag effect due to the reduction of Ce^{4+} to Ce^{3+}. [13] On the other hand, at high dopant concentrations, the average grain sizes of CGO10 and CGO30 are as small as ~0.46 μm and 0.30 μm, respectively, when sintered in air. These are much smaller than CeO_2 and CGO0.1 under the same condition. Such a microstructure with limited grain size is expected for highly doped ceria, where mass diffusion is strongly limited by the dopant solute drag effect. [13, 14, 18] Particularly in the case of nanometric powders with high dopant content, the solute drag phenomena can have a more severe pinning effect on the grain growth, as nano-sized powders have large volumes of grain boundary. [19] The effect of mass diffusion under reducing condition on the microstructure and specifically on the grain growth of CGO10 and CGO30 is illustrated in **Fig. 2f** and **h**. Comparing with the same samples sintered in air (**Fig. 2e** and **g**), the grain growth in 9% H_2-N_2 led to much larger grains, ~2.6 μm and 3.4 μm for CGO10 and CGO30, respectively, indicating enhanced mass diffusion in highly doped ceria under reducing condition. The solute drag effect observed in air (**Fig. 2e** and **g**) was not limiting the grain growth in highly doped ceria under reducing condition (**Fig. 2f** and **h**). Therefore, although with opposite effects, both the inhibited mass diffusion in low doped ceria and the enhanced mass diffusion in highly doped ceria are due to the same process: the chemical reduction of Ce^{4+} to Ce^{3+} determines the cation diffusion by a balance of charge and steric interactions. Such effects are controlled by the concentration of the dopant Gd^{3+} which determines the solute drag at the materials.

Fig. 1 Shrinkage (left side) and shrinkage rate (right side) curves from dilatometry of Gd-doped CeO_2 pellets (CeO_2, CGO0.1, CGO10 and CGO30) sintered in either air or reducing atmosphere (9% H_2-N_2) with a heating rate of 3°C/min.

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Fig. 2 SEM images of CeO$_2$, CGO0.1, CGO10 and CGO30 compacts after sintering in air and 9% H$_2$-N$_2$ at 1400 °C for 4h.

The microstructure in doped ceria is known to have a relevant effect on the electrochemical properties and especially on the total ionic conductivity of the materials. [9, 11] Particularly, the conductivity of the samples can change as result of the grain size and porosity, where these usually lead to blocking of the oxygen defect migration in the conduction process. [18] To characterize the effect of the treatment on the electrochemical properties, electrochemical impedance spectroscopy (EIS) measurements were performed on the samples treated at the TMA (**Fig.1** an **Fig.2**) with a frequency response analyzer (Solartron 1260, UK) in the temperature range 250–750 °C in static air, in the frequency range of 10^7 to 1 Hz, 100 mV ac voltage amplitude applied and zero *dc* bias. Both platinum and silver electrodes were used for the measure. [9, 11] The electrical conductivity was determined by fitting EIS diagrams normalized by the samples geometric factors. **Fig.3** shows the results expressed as Arrhenius plot of the total conductivity. This indicates that despite the slight microstructural differences measured in the different samples, all the materials sintered in reducing conditions have higher conductivity compared to the same compositions sintered in air. Such an effect is particularly relevant for the pure ceria which remarkably shows a total conductivity comparable with the highly doped samples. Another interesting result is about the performances of the CGO30 sample in reducing conditions which shows higher conductivity than the CGO10 sample treated in air. This result is also unexpected due to the fact that high dopant concentration is usually indicated as the promoter of blocking effects such as vacancies association and segregations. [18] However, according to the hypothesis that dopant is not preferentially segregated at the grain boundary in the solid solutions with
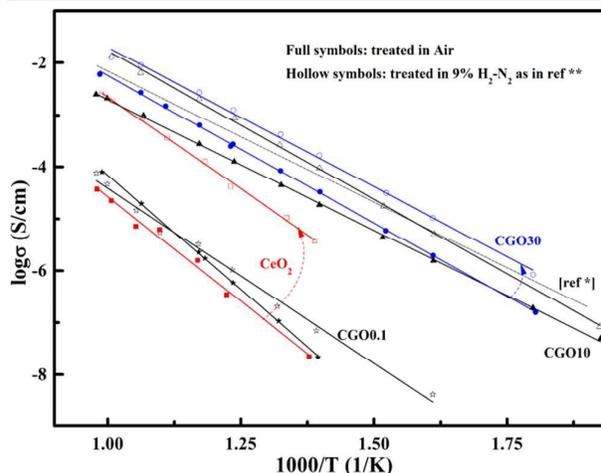
Fig. 3 Arrhenius plots for the total conductivity in air calculated by EIS data of CeO$_2$, CGO0.1, CGO10 and CGO30 compacts sintered in air and 9% H$_2$-N$_2$ at 1400 °C for 4h. The result of CGO10 sintered at 1050 °C in 9%H$_2$-N$_2$ is also shown for reference. [9]
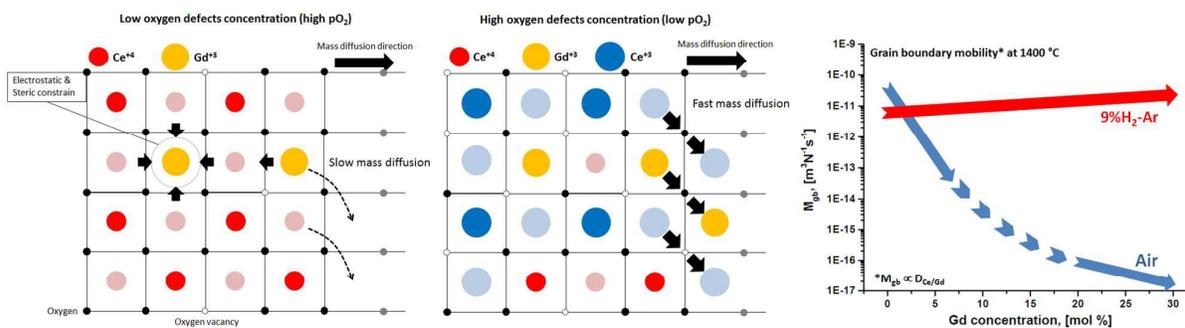
dominant Ce^{3+}, Gd cations are expected to be evenly distributed in the highly doped samples treated in reducing conditions because the cations are all similar in size and valence. This can thus have a beneficial effect on the electrical performances of these samples. On the other hand, the high conductivity in the pure CeO$_2$ sample treated in reducing conditions can be possibly explained by assuming that a certain amount of Ce^{3+} is still in solid solution and it acts as a dopant in the solid solutions. This is despite the high temperature reoxidation has been carried out on the samples (1100 °C in air for 5 hours). Presence of electronic conductivity in pure ceria and in the CGO0.1 can be also excluded for the same reason and by the fact that the measurements are taken in air.

Conclusions

The mass diffusion in aliovalent (*i.e.* Gd in 0, 0.1, 10 and 30 mol%) doped ceria is investigated in this work. Since mass diffusion in ceria is drastically influenced by the solute drag effect, the combined effects of chemical reduction from Ce^{4+} to Ce^{3+} and Gd^{3+} dopant concentration results in significant variations of mass diffusion mechanisms. Especially, consistently to the solute drag theory, in highly defective ceria obtained at high temperatures (1400 °C) and low oxygen activity (10^{-31}< pO$_2$< 10^{-12}atm), these lead to opposite effects of inhibition of densification and grain growth in pure ceria and low dopant concentration (0.1 mol % Gd$_2$O$_3$) and fast densification and grain growth at high dopant concentration (10 and 30 mol% of Gd$_2$O$_3$). The final result of the thermal and chemical treatments is a set of solid solutions whose electrochemical properties do not depend on the microstructure or on the nominal dopant concentration.

Notes and references

1 A. Trovarelli, *Catal. Rev. Sci. Eng.,* 1996, **38**, 439.
2 B.C.H. Steele, *Solid State Ionics*, 2000, **129**, 95.
3 C. William and S. Haile, *Phil. Trans. R. Soc. A*, 2010, **368** 3269.
4 M. Mogensen, N.M. Sammes and G.A. Tompsett, *Solid State Ionics*, 2000, **129**, 63.
5 R. Korobko, A. Lerner, Y. Li, E. Wachtel, A.I. Frenkel and I. Lubomirsky, *Appl. Phys. Lett*., 2015, **106**, 042904.
6 S. Sanna, V. Esposito, J.W. Andreasen, J. Hjelm, W. Zhang, T. Kasama, S.B. Simonsen, M. Christensen, S. Linderoth and N. Pryds, *Nature Mater.*, 2015, **14**, 500.
7 S. McIntosh and R.J. Gorte, *Chem. Rev.*, 2004, **104**, 4845.
8 P. Furler, J.R. Scheffe and A. Steinfeld, *Energy Environ. Sci.*, 2012, **5**, 6098.
9 V. Esposito, D.W. Ni, Z.M. He, W. Zhang, A.S. Prasad, J.A. Glasscock, C. Chatzichristodoulou, S. Ramousse and A. Kaiser, *Acta Mater.*, 2013, **61**, 6290.
10 F. Teocoli, D.W. Ni and V. Esposito, *Scripta Mater.*, 2015, **94**, 13.
11 D.W. Ni, J.A. Glasscock, A. Pons, W. Zhang, A. Prasad, S. Sanna, N. Pryds and V. Esposito, *J. Electrochem. Soc.*, 2014, **161**, F3072.
12 F. Teocoli, D.W. Ni, S. Sanna, F.C. Fonseca and V. Esposito, *J. Mater. Chem. A*, 2015, submitted.
13 P.-L. Chen and I-W. Chen, *J. Am. Ceram. Soc.,* 1994, **77**, 2289; P.-L. Chen and I-W. Chen, *J. Am. Ceram. Soc.*, 1996, **79**, 1793.
14 D.W. Ni, C.G. Schmidt, F. Teocoli, A. Kaiser, K.B. Andersen, S. Ramousse and V. Esposito, *J. Eur Ceram. Soc.*, 2013, **33**, 2529; D.W. Ni, V. Esposito, S.P.V. Foghmoes and S. Ramousse, *J. Eur. Ceram. Soc.*, 2014, **34**, 2371; D.W. Ni, K.B. Andersen and V. Esposito, *J. Eur. Ceram. Soc.*, 2014, **34**, 3769.
15 M.P. Pechini, *U.S. Pat.* 1967, 3330697.
16 J.G. Li , T. Ikegami and T, Mori, *Acta Mater*., 2004, **52**, 2221.
17 J.A. Glasscock, V. Esposito, S.P.V. Foghmoes, T. Stegk, D. Matuschek, M.W.H. Ley and S. Ramousse, *J. Eur. Ceram. Soc.*, 2013, **33**, 1289.
18 V. Esposito and E. Traversa, *J. Am. Ceram. Soc.*, 2008, **91**, 1037.
19 J.L.M.Rupp, A.Infortuna and L.J.Gauckler, *Acta Mater.*, 2006, **54**, 1721; N.I. Karageorgakis, A. Heel, J.L.M. Rupp, M.H. Aguirre, T. Graule and L.J. Gauckler, *Adv. Funct. Mater.*, 2011,**21**, 532.

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Valence and size of cations influence mass diffusion and oxygen defects in ceria. Mass diffusion is limited by the Gd^{+3} dopant in oxidative conditions, where Ce^{4+} is the host cation, while it is unleashed in reducing conditions, where Ce^{3+} and Gd^{3+} have same charge and similar size. Solid solutions with enhanced electrochemical properties can be formed in controlled thermo-chemical conditions.