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Prediction and evaluation of sintering aids for Cerium Gadolinium Oxide

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Abstract

This paper presents dilatometry results for $Ce_{0.9}Gd_{0.1}O_{1.95}$, a common intermediate temperature solid oxide fuel cell electrolyte material, doped at the 1, 3, and 5 mol% level using nitrates. The results indicate that across all dopant nitrate levels, Cu, Co, Fe, Mn, Li, and Zn reduce the $Ce_{0.9}Gd_{0.1}O_{1.95}$ sintering temperature, while Ca, Mg, and Ni have little effect, and Al and K increase the sintering temperature. These results can be interpreted in terms of a Vegard's Slope quality factor analysis which uses a dopant's charge and size to rank its propensity to heterogeneous dope the material and/or segregate to the grain boundary as a separate phase. Further, this work shows that $Ce_{0.9}Gd_{0.1}O_{1.95}$ can be sintered to 99% density at a record-low temperature of 800 °C, using as little as 3 mol% lithium as a dopant.
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1. Introduction

1.1. General background

Of the many materials with the potential to be used as a Solid Oxide Fuel Cell (SOFC) electrolyte at intermediate temperatures of 500–700 °C, Cerium Gadolinium Oxide (CGO) has one of the highest ionic conductivities [1], allowing its use in stainless steel supported fuel cells [2,3]. However, the need to produce such cells economically remains an issue and has prompted studies into the use of dopants and nano-sized powders to reduce the 1200 °C traditionally required to densify CGO electrolytes [4–20].

In addition to a very large surface area that increases the driving force for sintering, nano-powders promote low temperature sintering because, as pointed out by Herring [21], smaller particle size allows densification to occur primarily via grain-boundary diffusion instead of lattice diffusion. Given that the flux of atoms along a grain boundary, J, may be written as:

$$J = MC\nabla\mu \tag{1}$$

where M is the atomic mobility along the grain boundary, C is the vacancy concentration, and $\nabla\mu$ (the gradient in the chemical potential between the particle necks and a free surface) is the driving force for sintering, dopants which increase one or more of these terms can, in principle, be used to lower the sintering temperature, here defined as the temperature at which a sample reaches 95% of the theoretical density under constant heating rate conditions and denoted T_{sinter}. Determining the exact manner in which a particular dopant acts can be complicated. For example, the formation of a liquid phase, which Kleinlogel and Gauckler [7] observe when CGO is doped with Co, could alter M and increase $\nabla\mu$ due to capillary effects. Dopant substitution into the near grain boundary region, which Chen and Chen [22] refer to as the undersized dopant effect and observe in Sc doped ceria, could alter M or C (especially if the dopant has a charge/size discrepancy with the host ions). Lastly, dopant segregation to the grain the boundaries could alter M due to the formation of a second phase (or by scavenging SiO_2

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impurities as seen by Zhang et al. [15]) or alter $\nabla\mu$ by changing the surface and interface energies.

1.2. Dopant selection

For an ultra-clean CGO powder such as the one used in this study, a dopant's effectiveness should simply be a matter of its ability to form a beneficial liquid phase and/or its ability to improve the CGO near grain boundary atom flux, assuming the aforementioned dopant mechanisms are the only active ones and any secondary phase present is highly mobile at elevated temperature so that it does not become the diffusion limiting species. For a dopant to form a liquid phase, it must segregate to the grain boundaries instead of dissolving in the bulk. A dopant's solubility in CeO_2 is inversely proportional to the square of a its "Vegard's Slope" and for CeO_2 Kim [23] showed the Vegard's Slope, X, can be described by the equation:

$$X = (0.0220r_i + 0.00015z_i) \quad (2)$$

where r_i is the difference in ionic radii between the dopant and Ce^{4+} in 8-fold coordination, and z_i is the difference in charge between the dopant and Ce^{4+}. Hong and Virkar [24] have developed a similar expression for the Vegard's Slope and Ranlov et al. [25] have shown the relationship between the Vegard's Slope and the solubility even holds for nearly insoluble CGO dopants. Due to the requirement that a liquid-forming dopant must possess a low solubility in the bulk, the dopants most likely to induce liquid phase sintering in CGO should be those with an absolute value of the Vegard's Slope $\gg 0$. That said, as may be the case for Si [26] and Al [4] as shown in Table 1, if the |Vegard's Slope| is too large, a second phase in which CGO is insoluble can form, preventing liquid phase sintering and forcing the system to sinter via the solid-state sintering mechanism observed for the pure material. (As noted by Kingery [27], one of the requirements for liquid phase sintering is that the solid phase be soluble in the liquid so that atom transport can occur.) Thus, dopants with moderate absolute values of the Vegard's Slope should be the most likely to induce liquid phase sintering in CGO, such as the known cases of Bi^{3+}[5] and Co^{2+}[6].

Furthermore, the idea of using the Vegard's Slope as a sintering aid quality factor extends beyond liquid phase sintering. Ideally, a sintering aid would both form a beneficial liquid phase and favorably alter the near grain boundary, solid-state atom flux as well. Chen and Chen [28] showed that in CeO_2, cations are the limiting diffusing species, which is understandable given the material's high oxygen mobility. They also suggest that undersized acceptor dopants increase the near grain boundary cation mobility by heterogeneously doping the host material. Heterogeneous doping increases the near grain boundary oxygen vacancy concentration (due to charge compensation and the preference of an undersized dopant to coordinate with fewer than 8 oxygen atoms) while expanding the oxygen coordination shells around the host cations. Unfortunately, the relative importance of dopant size versus dopant charge on the near grain boundary cation mobility has

Table 1
Vegard's Slopes of all dopants with commercially available nitrates

Name	8-fold coordinated ionic radius (Å)	Vegard's slope (x 100,000)	Previously studied as a CGO dopant in reference:
B^{3+}	0.44*	−131†	
Si^{4+}	0.54*	−95†	
Al^{3+}	0.69*	−77	[4]
Ni^{2+}	0.83*	−61	[7,10]
Ga^{3+}	0.77*	−59	[18]
Mn^{3+}	0.78*	−58•	[7,12,13,19]
Fe^{3+}	0.78	−57	[7,8,10,12,14,15,17,39]
Cu^{+}	0.92*	−56•	
Li^{+}	0.92	−56	
Cu^{2+}	0.89*	−48	[7,8,10]
Mg^{2+}	0.89	−48	
Co^{2+}	0.90	−45	[7-12,20]
Zn^{2+}	0.90	−45	[7,8,10]
Fe^{2+}	0.92	−41•	
Sc^{3+}	0.87	−37	
Mn^{2+}	0.96	−32	
Hf^{4+}	0.83	−31	
Zr^{4+}	0.84	−29	
In^{3+}	0.92	−26	
Lu^{3+}	0.98	−13	
Tl^{3+}	0.98	−13	
Yb^{3+}	0.99	−12	
Tm^{3+}	0.99	−10	
Er^{3+}	1.00	−8	
Pd^{2+}	1.08*	−6	
Ho^{3+}	1.02	−5	
Y^{3+}	1.02	−4	
Dy^{3+}	1.03	−2	
Cd^{2+}	1.10	−1	
Tb^{3+}	1.04	0	
Na^{+}	1.18	1	
Ca^{2+}	1.12	3	
Gd^{3+}	1.05	3	
Eu^{3+}	1.07	6	
Hg^{2+}	1.14	7	
Sm^{3+}	1.08	9	
Nd^{3+}	1.11	16	
Pr^{3+}	1.13	19	
Ce^{3+}	1.14	23	
Ag^{+}	1.28	23	
La^{3+}	1.16	27	[10]
Bi^{3+}	1.17	29	[5]
Sr^{2+}	1.26	34	[10]
Hg^{+}	1.34*	36	
Pb^{2+}	1.29	40	
Ba^{2+}	1.42	69	
K^{+}	1.51	74	
Tl^{+}	1.59	92	
Rb^{+}	1.61	96	
Cs^{+}	1.74	124	

* No 8-fold radii were listed in Shannon's [37] Table for these dopants. Radii were extrapolated from lower coordinations. All extrapolated dopants had entries for C.N. = 6.

† No commercially available dopant nitrate exists. Included for reference.

• Even though no dopant nitrates are commercially available, Mn^{3+} was included because $Mn(NO_3)_2$ decomposes to Mn_2O_3, Cu^{+} was included because CuO can be reduced at high temperatures, and Fe^{2+} was included because Fe_2O_3 can be reduced at high temperature.

Highlighted CGO dopants were studied in this paper.