

ENHANCED MASS DIFFUSION PHENOMENA IN HIGHLY DEFECTIVE DOPED CERIA: LIMITS AND APPLICATIONS

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Introduction

Cerium oxide is one of the most relevant materials in the class of electroceramics for energy conversion applications. Acceptor doped ceria, where the dopant A^{3+} is typically Gd, Sm, Y, Eu, Dy etc., is especially used as a fast conductor in solid oxide fuel cells and oxygen separation membranes. Due to its technological relevance, growing attention has been recently dedicated to the material processing, and particularly with respect to the sintering of dense layer in multi-layer constrained structures [1, 2]. In doped-fluorites, solute drag phenomena control the sintering: the dopant (solute) limits mass diffusion by electrostatic and/or elastic interactions “trapping” cations, especially at the grain boundary [3]. This work is dedicated to the investigation of sintering mechanisms in 10 mol.% Gd-doped CeO_2 ($Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$, GDC10) under low oxygen partial pressure, particularly focusing on the role of defects on free densification and grain growth, considering the influence of starting particle sizes and chemical expansion on the charge transport properties. Some examples on how fast mass diffusion phenomena influence microstructural stability and sintering process of the material are reported.

Experiments

Diffusivity of highly defective doped ceria in reducing conditions are measured by contact dilatometry and analyzing grain growth evolution by scanning electron microscopy (SEM). Structural and chemical investigation is carried out by transmission electron microscopy (TEM).

Results and Discussion

The densification and grain growth of the solid state ionic conductor material $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (*i.e.* GDC10, gadolinium doped-ceria Gd-10 mol. %) are analyzed for nanometric and fine powders of different particle size, both in air and in a 9 vol.% H_2-N_2 mixture. Due to a dominant solute drag effect in aliovalent highly doped ceria, the starting morphology of the powders controls the diffusion mechanisms (Fig. 1). Conversely, highly enhanced densification and grain growth are achieved by firing the materials at reduced temperatures ($800 < T < 1200$ °C) in low oxygen activity atmospheres ($pO_2 < 10^{-12}$ atm). Fast diffusion is activated under low oxygen activity with high grain boundary mobility. High densification and electric conductivity are achieved in $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ at low temperatures (~ 1000 °C) and low oxygen activity. The large chemical expansion

associated with a high defect concentration during sintering can be controlled to avoid catastrophic stress conditions during reoxidation at low temperatures.

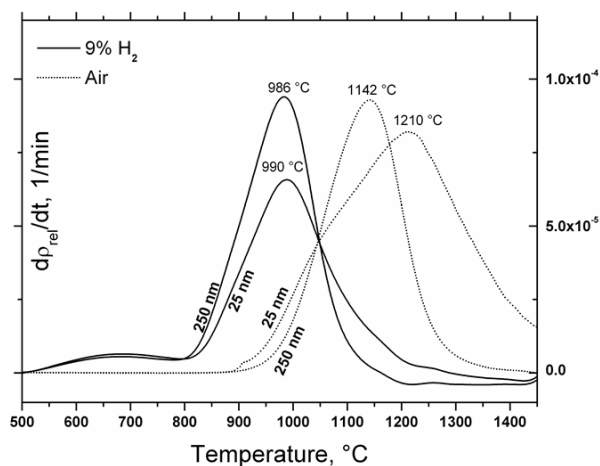


Fig. 1. Dilatometry data for samples with starting particle size 25 and 250 nm sintered in 9% H_2-N_2 and in air expressed as densification rate with temperatures.

Conclusions

Fast cation diffusion is achieved in highly defective $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ ($\delta \approx 0.2$) as a result of Ce/Gd cation average equivalence in the fluorite structure. As a consequence, mass diffusion mechanisms lead to drastic microstructural changes at much lower temperatures for samples treated in a reducing atmosphere as compared to air. Full densification and fast grain growth in GDC10 powder compacts can be achieved by sintering under low pO_2 ($< 10^{-12}$ atm). The solute drag effect is not limiting either the densification or the grain growth under reducing conditions and the starting powder properties had a minor role in the sintering process.

References

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