Effect of Doping with Co$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, and Mn$_2$O$_3$ on the Properties of Ce$_{0.8}$Gd$_{0.2}$O$_2$ – δ


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Received July 7, 2006; in final form, December 19, 2006

Abstract—The effects of Co, Fe, Mn, and Ti oxide additions on the sinterability and crystal-chemical, thermal, and electrical properties of Ce$_{0.8}$Gd$_{0.2}$O$_2$ – δ have been studied. The results indicate that these oxides enhance the sinterability of the mixed oxide, regardless of whether they were introduced before or after synthesis. The most effective sintering aid is Co$_2$O$_3$. The lattice parameters of Ce$_{0.8}$Gd$_{0.2}$O$_2$ – δ samples containing different metal oxide additions (1 mol %) are refined in space group Pm3m. The temperature-dependent thermal expansion data are used to determine the linear thermal expansion coefficients of the samples. Manganese oxide additions reduce the electrical conductivity of Ce$_{0.8}$Gd$_{0.2}$O$_2$ – δ, whereas the other dopants increase it in the order Ti < Fe < Co. The activation energy for conduction increases in the order Co < Ti < Fe < Mn.

DOI: 10.1134/S002016850707070126

INTRODUCTION

Materials based on gadolinium-doped ceria, Ce$_{1−x}$Gd$_x$O$_{2−δ}$, are currently the most attractive electrolytes for medium-temperature solid oxide fuel cells [1, 2]. At temperatures below 1070 K, these materials possess high ionic conductivity, which exceeds the conductivity of zirconia by a factor of 4–5 [3]. In addition, they offer low activation energy for conduction [4] and high catalytic activity [5]. The major drawback to Ce$_{1−x}$Gd$_x$O$_{2−δ}$ materials is their poor sinterability. The sintering temperature of Ce$_{1−x}$Gd$_x$O$_{2−δ}$ prepared by a conventional ceramic processing technique can be as high as 1970 K [6]. There are several possible approaches to this problem. The most common approaches are to utilize various synthetic techniques: oxalate coprecipitation [7], nitrate decomposition [8], Pechini process [9, 10], sol–gel processing [3], and CO$_2$ laser ablation [11]. These processes make it possible to reduce the initial particle size, thereby enhancing the sinterability of the material. They, however, have a number of drawbacks: high cost of the starting materials, complex procedure, and low yield of the desired product. An alternative approach proposed by several researchers for reducing the sintering temperature of ceria-based solid solutions is to introduce small amounts of additives capable of improving the sintering behavior of the material. For example, the addition of 1 at % manganese to CeO$_2$ enables a 99.0% relative density to be achieved by sintering at 1570 K for 2 h [12]. The introduction of 1% manganese into Ce$_{0.8}$Gd$_{0.2}$O$_2$ – δ was reported to reduce its sintering temperature from 1790 to 1618 K (the initial particle size of the powder was 0.1 μm) [13]. Using 2 mol % cobalt oxide additions, Kleinlogel and Gauckler [14] sintered Ce$_{0.8}$Gd$_{0.2}$O$_{2−δ}$ nanopowder to a 99.0% relative density at temperatures from 1170 to 1370 K. In spite of the reduced sintering temperature, the grain size of the sintered material was in the submicron range (120 nm), and the material had improved mechanical properties. Moreover, cobalt additions were reported to raise the electrical conductivity of Ce$_{0.8}$Gd$_{0.2}$O$_{2−δ}$ and to reduce its activation energy [15]. The objective of this work was to study the effect of different additives (Co, Fe, Mn, and Ti) on the sinterability and crystal-chemical, thermal, and electrical properties of Ce$_{0.8}$Gd$_{0.2}$O$_{2−δ}$.

EXPERIMENTAL

Ce$_{0.8}$Gd$_{0.2}$O$_{2−δ}$ samples for this investigation were prepared via ceramic processing route. The final heat-treatment step was carried out at 1570 K in air. The starting chemicals used were extrapure-grade ceria, CeO$_2$, and gadolinia, Gd$_2$O$_3$. As sintering aids, we used analytical-grade Mn$_2$O$_3$ and Fe$_2$O$_3$, pure-grade Co$_2$O$_3$, reagent-grade TiO$_2$, and extrapure-grade cobalt nitrate, Co(NO$_3$)$_2$ · 6H$_2$O. Sintering aids can be introduced into Ce$_{0.8}$Gd$_{0.2}$O$_{2−δ}$ both during synthesis, in the form of oxides [12, 13, 16], and after synthesis, in the form of nitrates [14, 15, 17]. To compare these approaches, cobalt was introduced both during Ce$_{0.8}$Gd$_{0.2}$O$_{2−δ}$ synthesis (procedure I) and after the synthesis (procedure II).

To introduce a sintering aid by procedure I, appropriate
amounts of the constituent oxides of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ and a metal oxide (1 at% in the oxide mixture) were mixed by ball milling in ethanol for 0.5 h in a Fritsch Pulverisette-6 planetary mill, following which solid-state synthesis was performed. In procedure II, presynthesized $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ was mixed with cobalt nitrate by ball milling with ethanol for 0.5 h in the Pulverisette-6, and the mixture was then calcined at 670 K for 2 h. Ti, Fe, and Mn additions were introduced by procedure I. The synthesized powders were ground for 2 h under ethanol in the Pulverisette-6 (polyurethane vials and tetragonal zirconia grinding media) at a powder : ball : ethanol weight ratio of 1 : 5 : 1. The specific surface area of the starting materials and the particle size distribution were determined by BET measurements with a Shimadzu SA-CP2 particle size analyzer.

Bar-shaped samples for property measurements, $0.2 \times 0.3 \times 2 \text{ cm}$ in dimensions, were prepared by semi-dry pressing at 229 MPa with the addition of a 5% ethanolic solution of poly(vinyl butyral). The green compacts were sintered at temperatures from 1670 to 1970 K via heating at a rate of 2.5 K/min and holding at the sintering temperature for 180 min, followed by cooling to room temperature at 1.5 K/min.

The phase composition and lattice parameters of the samples were determined by x-ray diffraction (XRD).