

Master sintering curve for Gd-doped CeO₂ solid electrolytes

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Abstract The sintering behavior of gadolinia-doped ceria powders was studied by the master sintering curve (MSC). Dilatometric analyses of powders produced by a soft chemical method were performed to provide the experimental data set for the construction of the MSC. The assumed model provided good fittings of the MSC and the activation energy for the sintering of Ce_{1-x}Gd_xO_{3-δ}, with $x = 0, 0.05, 0.1, \text{ and } 0.2$ were found to be in the 218–325 KJ/mol range, depending on the dopant content. The results supported that both the nanometric size of the particles and the difference in ionic radii between Gd³⁺ and Ce⁴⁺ affects the sintering of Gd-doped CeO₂.

Keywords Master sintering curve · Ceria · Solid electrolyte · Solid oxide fuel cell · IT-SOFC

Introduction

Solid Oxide Fuel Cells (SOFC) convert directly the electrochemical energy of a fuel to electric energy and heat. Such devices have been considered as a potential high efficiency and sustainable power source. The reduction of

the operation temperatures of SOFC has been drawing a great deal of attention due to several advantages like: wider choices of low cost and high performance component materials, higher stability, and reduced degradation. CeO₂-based electrolytes have been widely studied for prospective applications in electrochemical devices, including SOFC, operating at intermediate temperature (500–750 °C) due to their superior ionic conductivity as compared to the standard yttria-stabilized zirconia (YSZ) [1]. The most effective additives of ceria for high ionic conductivity are Gd₂O₃ and Sm₂O₃, possibly because they minimize the changes in net lattice parameters. However, differences in ionic radii between Gd³⁺, Sm³⁺, and Ce⁴⁺ can affect diffusion processes involved in sintering mechanisms [2, 3].

The ability to predict sintering behavior has been one of the long term objectives of sintering studies for many decades. It is well understood that the sintering behavior of any particular material depends upon several characteristics of the powder, including composition, particle size, size distribution, particle shape, degree of agglomeration and other factors [4]. The sintering control could lead to several advantages such as multi-materials process design or co-processing, materials integration, co-sintering, dimensional, microstructure, density and quality control. In the case of SOFC significant efforts have been dedicated for the optimization of cell production by co-sintering electrode/electrolyte layers. Effective sintering processes are considered an important step in the cell production affecting both the SOFC performance and its costs.

In order to better understand the sintering of ceramics the construction of a Master Sintering Curve (MSC) has been proposed [4]. The MSC can be used to predict the densification behavior of a given powder and estimates its minimum sintering activation energy. For the construction of MSC the parameters of sintering are separated in those

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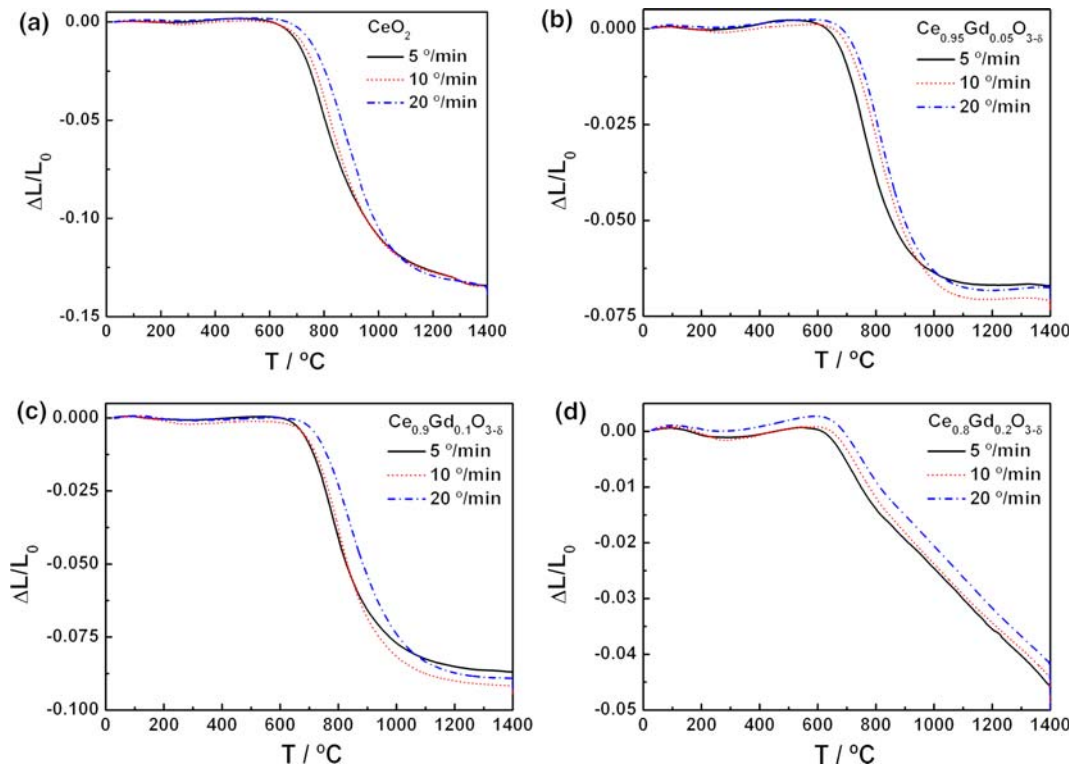


Fig. 1 Linear shrinkage for $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ samples at different heating rates

related to time and temperature dependence and the ones associated with the microstructure. The combined stage sintering models relates the linear shrinkage rate of a compact at any given instant to the grain boundary and volume diffusion coefficients, the surface tension and certain aspects of the instantaneous microstructure of the compact. According to the literature [5] the linear shrinkage rate is related to the densification rate. Consequently, the MSC can be generated from the measured densities as a function of Θ parameter defined by the equation [5]:

$$\Theta = \frac{1}{c} \sum_{T_0}^T \frac{1}{T} e^{-E/RT} \Delta T \quad (1)$$

where c is the heating rate, T the absolute temperature, T_0 is the absolute initial temperature, E the activation energy, R is the gas constant and ΔT the temperature variation.

A convenient procedure for the construction of the MSC consists in collecting linear retraction data with different constant heating rates. The final densities are measured for each heating rate and the density during retraction is calculated from the linear shrinkage data. With these set of data the value of Θ is computed for each experimental value using an assumed value of the activation energy (E). Then, data from each heating rate are plotted simultaneously as density versus $\log \Theta$ and

fitted with a proper function usually a sigmoid. If a large χ_{reduced}^2 value is obtained, then the activation energy may be inappropriate and the fitting must be repeated with more suitable activation energy (E) value that minimizes χ_{reduced}^2 [5].

In the present study, master sintering curves have been calculated for gadolinia-doped ceria nanopowders produced by a soft chemical method. The experimental results evidenced the high sinterability of the powders, and a dependence of the sintering activation energy on the gadolinia content was observed.

Experimental

$\text{Ce}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$, with $x = 0$ (pure ceria), 0.05, 0.10 and 0.20 nanometric powders were prepared using a diamine assisted co-precipitation method in aqueous solution. Details of the preparation method are found elsewhere [3]. Starting powders were calcined at 450 °C for 6 h. Cylindrical pellets (5 mm diameter and approximately 10 mm thickness) were produced by uniaxial cold pressing at 150 MPa in a stainless steel die.

Green compacts were analyzed in a dilatometer (Setaram Labsys) up to 1,400 °C with 5, 10, and 20 °C/min heating rates in flowing nitrogen (40 mL/min).

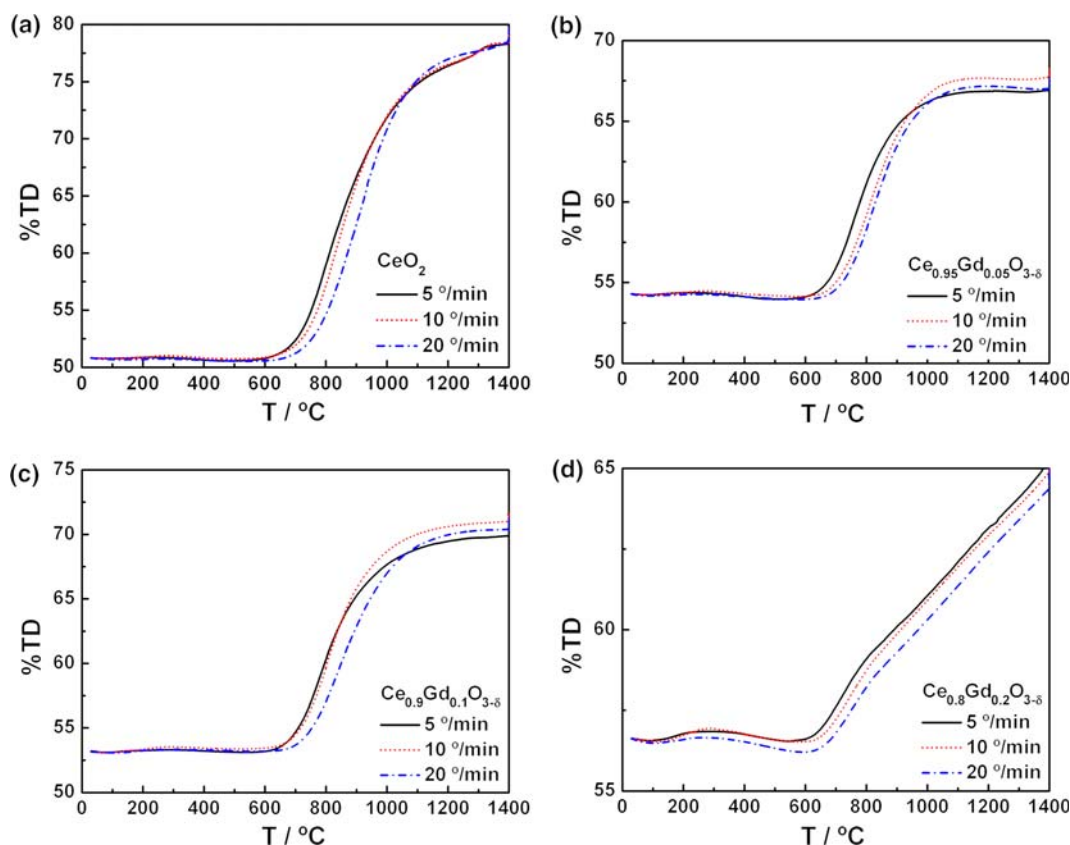


Fig. 2 Temperature dependence of the percentage of theoretical density (%TD). The %TD values were determined using Eq. 2

Results and discussion

Figure 1 shows the normalized linear shrinkage versus temperature for Ce_{1-x}Gd_xO_{3-δ} samples.

Typical features of the sintering of ceramic samples are inferred from data displayed in Fig. 1. The gadolinia-doped ceria powders exhibit onset of linear shrinkage at ~600 °C, maximum densification rate at ~750 °C and total linear shrinkage at temperatures ≥1,100 °C. No significant dependence of both the onset of linear shrinkage and the maximum densification rate temperature on the dopant content was observed. However, increasing the Gd content increases the total linear shrinkage temperature and the sintering of the x = 0.20 sample was not completed up to 1,400 °C. Usually, sintering aids are added to ceramic materials in concentrations rather lower than that used for optimized ionic conductivity in the present study. The dilatometry analyses indicate that high contents of the dopant ion retard the final sintering stage (pore elimination) of Ce-based samples. The main effect of varying the heating rate, between the 5 and 20 °C/min, was a shift of dilatometric curves to higher temperatures, markedly in the 500–1,000 °C temperature range.

The normalized shrinkage values were converted into percentage of theoretical density (%TD) according to the relation:

$$\%TD = \frac{100[L_0 / (dL + L_0)]^3 \rho_0}{\rho_t} \tag{2}$$

where L₀ is the initial sample length, dL the linear shrinkage variation, ρ_t the theoretical sample density and ρ₀ is the initial sample density.

Using the calculated values of %TD, dilatometric data were re-plotted as %TD versus temperature, as shown in Fig. 2.

The addition of Gd to ceria promotes an increase of the initial (green) density values and for intermediary Gd concentration, Ce_{1-x}Gd_xO_{3-δ} with x = 0.05 and 0.10, the total linear shrinkage was attained at lower temperatures (1,200–1,300 °C) than that of the undoped sample. However, samples containing 20 at.% of Gd (Ce_{0.8}Gd_{0.2}O_{3-δ}) sintered at 1,400 °C present lower final density.

The %TD versus log Θ curves obtained by using Eq. 1 for all heating rates and arbitrarily chosen sintering activation energies (E) were fitted to a sigmoidal function [4]:

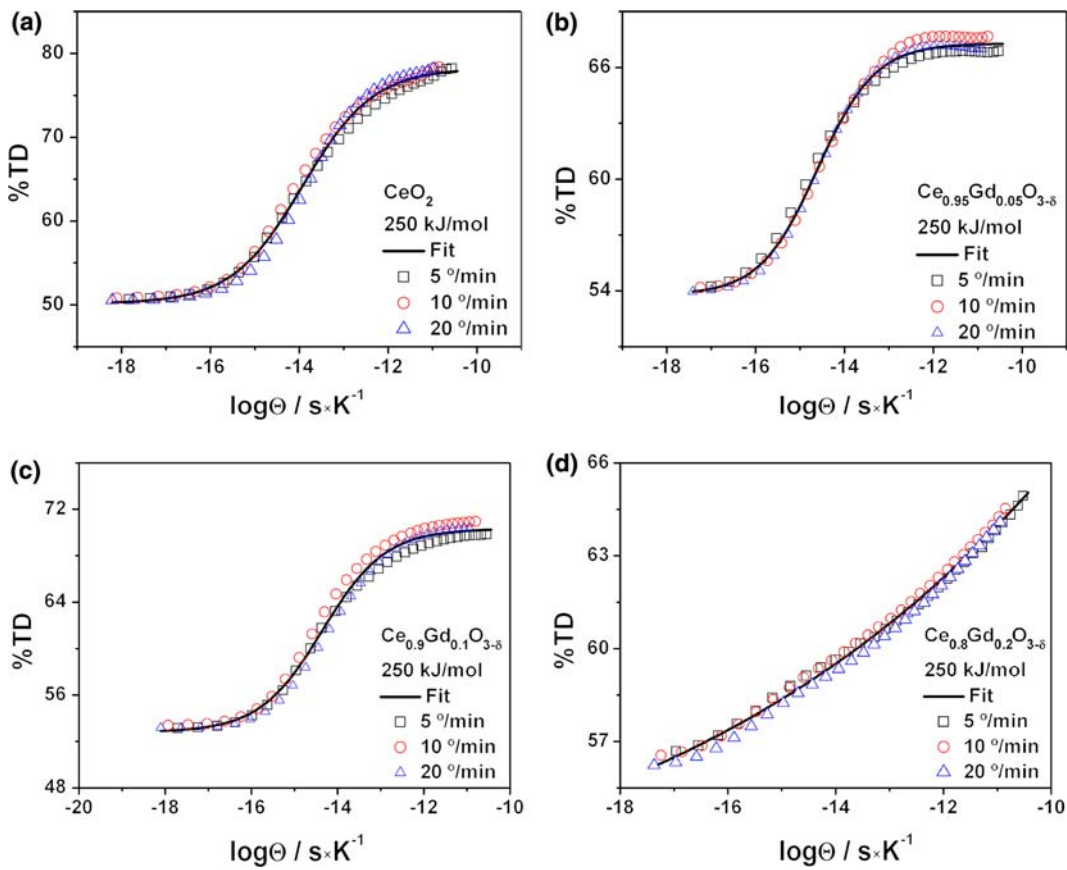


Fig. 3 $Ce_{1-x}Gd_xO_{3-\delta}$ master sintering curves for activation energy of 250 kJ/mol

$$\%TD = \frac{\%TD_i - \%TD_f}{1 + \exp\left[\frac{(\log \Theta - \log \Theta_0)}{\Delta \log \Theta}\right]} \%TD_f \quad (3)$$

where %TD_i and %TD_f are initial and final %TD values and log Θ₀ is the curve inflection point value.

Figure 3 shows examples of sigmoidal fittings assuming an activation energy of 250 kJ/mol in Eq. 1. The MSC model collapses the experimental data taken at different heating rates into a single curve, which is well described by Eq. 1.

The quality of fittings displayed in Fig. 3 was evaluated by the $\chi^2_{reduced}$, and the fitting procedure was repeated for different activation energy values. The computed $\chi^2_{reduced}$ and corresponding energy values were plotted, as displayed in Fig. 4. The minimum $\chi^2_{reduced}$ was associated with the activation energy for sintering of Gd-doped ceria powders, and the obtained values are listed in Table 1.

The activation energies calculated for $Ce_{1-x}Gd_xO_{3-\delta}$ samples are within the range of energy values reported for doped ceria ceramics [6–9]. Small variations can be attributed to both the nature and content of dopant cations used in previous studies [6–9]. In addition, different particle sizes of starting powders are known to strongly affect the sintering process. In a recent study, the MSC model

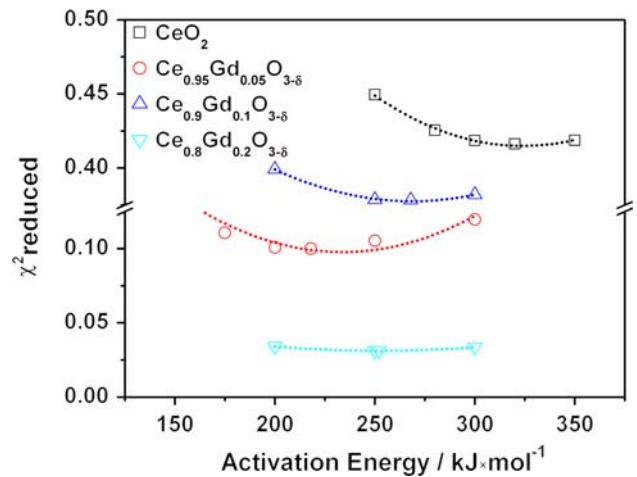


Fig. 4 Fitting quality parameter ($\chi^2_{reduced}$) for different activation energy values

was applied to calculate the sintering activation energy of both nano- and sub-micrometer CeO_2 particles [9]. In that study [9], the calculated activation energies for nano- and sub-micrometer powders were 370 and 440 kJ/mol, respectively. In the present study, the chemical synthesis

Table 1 Sintering activation energy for the Ce_{1-x}Gd_xO_{3-δ} samples

Sample	<i>E</i> (kJ/mol)
CeO ₂	325
Ce _{0.95} Gd _{0.05} O _{3-δ}	218
Ce _{0.9} Gd _{0.1} O _{3-δ}	268
Ce _{0.8} Gd _{0.2} O _{3-δ}	252

resulted in average particle sizes in the 10–15 nm range, as inferred by microscopy analyses [3]. The produced Ce_{1-x}Gd_xO_{3-δ} nanoparticles have higher sinterability and higher surface energy than coarser particles reported in [9]. Such a feature is probably associated with the relatively lower (~45 kJ/mol) values found for the sintering activation energy in the present study.

Conclusions

The activation energy for the sintering of high surface area Ce_{1-x}Gd_xO_{3-δ}, with *x* = 0, 0.05, 0.10 and 0.20, produced by a soft chemistry method was calculated by using the master sintering curve model. Good fittings to experimental data resulted in activation energy values in the 218–325 KJ/mol range, depending on the Gd doping content, and in agreement with previous reported data for ceria based oxides. The activation energies calculated for doped-ceria samples are lower than that calculated for CeO₂ evidencing that both the difference in ionic radii between Gd³⁺ and Ce⁴⁺ and the initial particle size affects the

sintering mechanism. The master sintering curve allows for the prediction from the early to the final stages of sintering, and can be useful for the processing of Gd-doped ceria electrolyte and/or anodes for solid oxide fuel cells.

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