Supplementary Information

Tuning diffusion paths in shaped ceria nanocrystals

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1. Evolution of the crystallites size characterization by XRD

**Figure S1.** XRD data for NCs (a) and NRs (b) showing reflections (111), (220), and (311) used for calculating crystallite size measured at room temperature (RT) for the as-synthesized materials and after heat treatments in air at 850, 1050, and 1400 °C for 0.1 h. Inset tables show average crystallite size for each temperature.

The thermal evolution of crystals was studied by the temperature dependence of the crystallite size. XRD data for both NRs and NCs as-synthesized (room temperature) and heat treated at 850 and 1050 °C, corresponding to the peaks observed in SSD activity shown in Fig. 2a of the manuscript, were used calculate the crystallite size. Average crystallite size was calculated from 111, 220 and 311 reflections of GDC diffraction patterns shown in Fig.S1. Along with values obtained for samples sintered at 1400 °C, the calculated size (standard deviation ~15%) reflect the results discussed in the manuscript. As-synthesized NRs have 17nm crystallite size that increases
fast with increasing temperature, reaching ~50 nm at 850°C and 62 nm at 1400 °C. Such a crystallite size is comparable to the one calculated for NCs. However, the slow solid state mass diffusion of NCs is mirrored on the practically temperature-independent crystallite size (~60 nm) of all measured samples. To further advance the understanding of the influence of particle shape on the properties of sintered GDC samples, XRD data was further related to the microstructural observation of samples sintered at intermediate temperatures.

2. Evolution of morphology at differential diffusive steps.

![SEM observations of NCs (left) and NRs samples (right) treated at 800 °C (top) and 1100 °C (bottom) in air for 0.1 hours.](image)

Figure S2. SEM observations of NCs (left) and NRs samples (right) treated at 800 °C (top) and 1100 °C (bottom) in air for 0.1 hours.

Figure S2 shows the SEM pictures of the NCs (left) and NRs samples (right) sintered for 0.1 hours in air at 800 °C (top) and 1100 °C (bottom). Temperature of heat treatments were selected to characterize the effect of the mass diffusion activated at intermediate stages. The short holding time, i.e. 0.1 hour, was used to represent the intermediate stages for NRs at the early stage of the mass diffusion. As shown in Figure 2a, these temperatures correspond to a first set of low temperature diffusion mechanism for the samples (see first peak at ca. 800°C in Figure 2a bottom)
and to a second set of activities at higher temperatures before densification (second peak at ca. 1100 °C in Figure 2a bottom) of the NRs sample. For the NCs samples, the dilatometry showed that no densification activity was measured along the different temperatures.

Figure S2 clearly shows that mass diffusion in NCs is very limited at low temperatures, as the sample at 800 °C possess similar microstructural features of those of the as synthesized sample (see Figure 1). Conversely for the NRs sample, the treatment at 800 °C shows a rapid change of the rod shape (Figure 1) into spheroidal nanoparticle with average size of 30 nm (Figure S2 top-right), where only few particles maintain the rod-like shape. Treatments at 1100 °C led to grain growth from 30 nm to 100 nm. Consistently with results shown in figure 2, the NRs sample also exhibited residual porosity that is annihilated during densification at temperatures above 1100 °C. For the NCs samples, the microstructural evolution at 1100 °C presents interesting features. Consistently to results in Figure 2, no sign of densification are observed while SEM in S2 and shows that crystals maintain the same size. The only signs of mass diffusion detected at 1100 °C deal with a smoothing of edges and coroners at the cubes, suggesting a process of spheroidization of the crystals, toward the microstructural features observed at 1400 °C (see figure 2).