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SANS investigation on evolution of pore morphology for varying sintering time in porous ceria

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Abstract. Precipitates of ceria were synthesized by homogeneous precipitation method using cerium nitrate and hexamethylenetetramine at 80°C. The precipitates were ground to fine particles of average size ∼0.7 μm. Circular disks with 10 mm diameter, 2 and 3 mm thickness were prepared from the green compacts by sintering at 1300°C for three different sintering times. Evolution of the pore structures in these specimens with sintering time was investigated by small-angle neutron scattering (SANS). The results show that the peak of the pore size distribution shifts towards the larger size with increasing sintering time although the extent of porosity decreases. This indicates that finer pores are eliminated from the system at a faster rate than the coarser ones as sintering proceeds and some of the finer pores coalesce to form bigger ones.

Keywords. Ceramics; neutron scattering; porosity.

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1. Introduction

Porous ceramics find many important technological applications in catalytic systems, sensors and gas burners. Since pores are used as second phase to design materials with tailored properties, it often becomes necessary to control pore volume fraction as well as pore size. For many catalytic applications, host materials need to be permeable and the processing emphasis is often focussed on how to control the size of the pores. The porosity can also decrease the dielectric constant of a ceramic while higher dielectric constant is desired in substrates used for microelectronics [1].

Ceria (CeO_2) is one such material, used for some of the above applications. Especially gas permeable porous ceria bodies made from ultra-fine powders find application as hosts for catalysts in automobile exhaust. It has been observed that by suitably tailoring the sintering conditions (temperature, time and pressure) total porosity and the pore size distribution can be varied [2].

Small-angle neutron scattering (SANS) is a nondestructive technique [3] to characterize pore structure in various porous materials [4–6] in the length scale ranging

from 1 to 1000 nm. A study of the role of the sintering conditions on the pore size evolution in ceria is essential for optimizing the final porosity and average pore size for desired applications. In this paper SANS investigation on pore structure of ceria specimens sintered at varying time is presented.

2. Experiments

2.1 *Sample preparation*

Cerium hydroxide was obtained by homogeneous precipitation reaction using aqueous solution of cerium nitrate (0.05 M, 99.9% purity) and hexamethylenetetramine (0.5 M, 99.5% purity) at 80°C. The precipitates were filtered and washed with water and alcohol and then dried in oven at 70°C. The dried precipitates were calcined at 600°C to obtain pure ceria and ground planetarily to a mean size of 0.7 μm. The mean particle size of the powder (figure 1) was determined using the laser light scattering technique (Master sizer 2000, M/s Malvern, UK). Powder compacts with thickness in the range of 3–4 mm and diameter 16 mm were cold pressed and sintered at 1300°C in a super kanthal furnace for varying time (15, 30 and 120 min). Bulk density of the compacts was measured by water immersion technique. The densities of the sintered pellets were found to be 74%, 85% and 93% respectively of theoretical density (TD) indicating the gradual decrease of the total porosity.

2.2 *SANS experiments*

Experiments have been carried out on these pellets using the double crystal diffractometer [7] at the Guide Tube Laboratory of Dhruva reactor, Trombay. Scattered

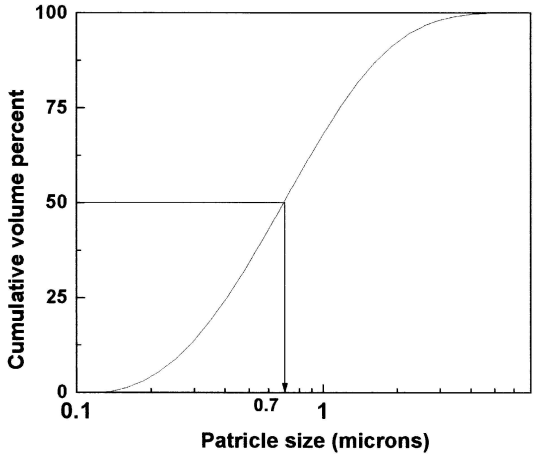

Figure 1. Particle (CeO_2 powder) size distribution.

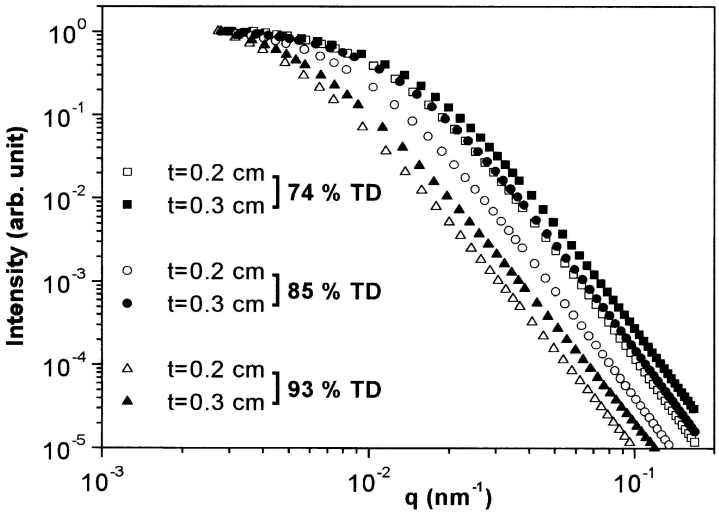

Figure 2. Resolution-corrected SANS profiles.

intensity data were collected in the accessible range ($\sim$0.003 – 0.173 nm^{-1}) of the scattering vector $q = (4\pi \sin\theta)/\lambda$, where 2θ is the angle of scattering, λ(= 0.312 nm) being the wavelength of the incident neutrons. Resolution corrected intensity profiles are shown in figure 1. SANS profiles for two values of thickness (2 mm and 3 mm) of each specimen were recorded to correct for the effect of multiple scattering [8,9].

3. Results and discussion

It is evident from figure 2 that the profiles become sharper with the increase in sintering time. To have an idea on the linear extent of the pores, the radius of gyration (R_g) is determined from the slope of log (intensity) vs. q^2 plot at very low q region (i.e. Guinier region) of the profiles. The radii of gyration have been calculated from all the profiles (figure 3). It is found that a temporal power law with exponent $\sim$0.4 fits with the growth. It is noteworthy that computer simulation [10] on porous ceramics predicts that a power law with time exponent 0.2 governs the growth kinetics of mean pore size. However, as the effective radius of gyration for a polydispere population of spherical pores is related to the square root of the ratio of the eighth moment to the sixth moment of the pore size distribution an exponent greater that 0.2 is expected and hence the growth of radius of gyration. The single scattering profiles (SSP) have been extracted from the profiles obtained for two values of thickness of each specimen. The extracted SSPs have been fitted with polydisperse spherical pores model to estimate the pore size distribution (figure 4).

The estimated pore size distributions are depicted in figure 5. The distribution shifts towards the higher radius side with increase in sintering time. We further notice that for longer sintering time the lower end tail of the distribution is signifi-

cantly reduced. This indicates that the finer pores are eliminated from the system at a faster rate than the coarser ones and the coalescence of some of the smaller pores could also have resulted in the formation of bigger pores. This could be explained in the following way. In the initial stage of sintering, necks grow between contacting particles. As sintering proceeds, necks emerge and bigger grains form. As the distance at which mass transport has to take place during sintering is less for finer pores, the kinetics of their elimination is faster than that of the coarser ones. As an indirect consequence of the mass transport, the migration of the small pores also takes place and they coalesce to form bigger pores [11].

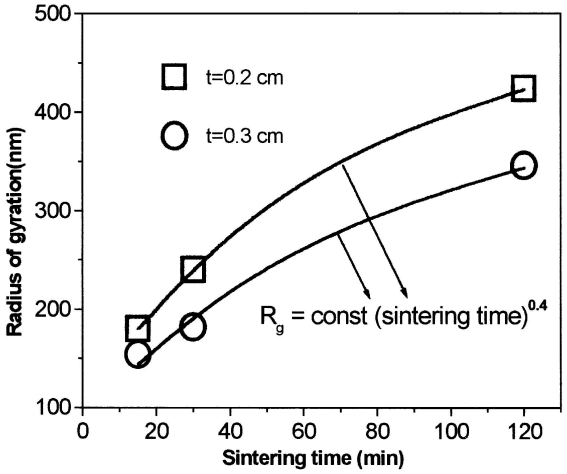

Figure 3. The evolution of the radius of gyration with sintering time.

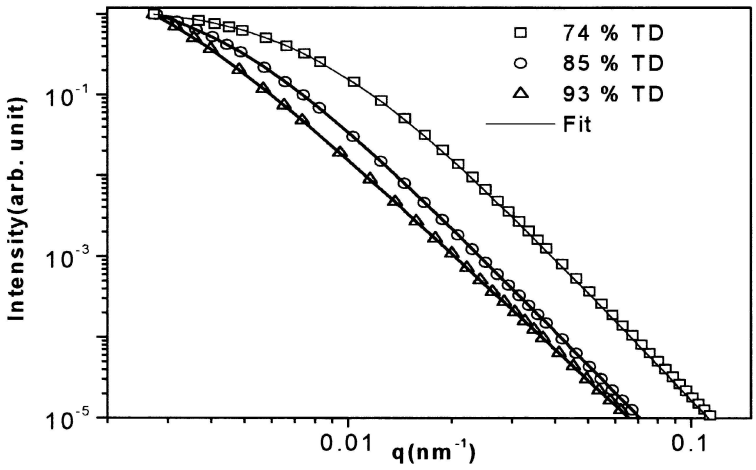

Figure 4. Fit of the model to the extracted single scattering profiles for three sintering.

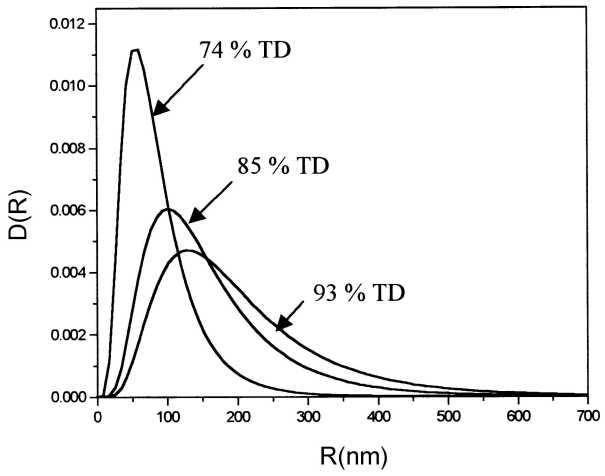

Figure 5. The estimated pore size distribution.

4. Conclusions

SANS investigation shows shifting of the pore size distribution to the higher radius side with the increase in sintering time although decrease in the porosity occurs due to the elimination of the pores from the system. This phenomenon is explained because of two factors. As the distance of mass transport for sintering is less in case of fine pores, the kinetics of their elimination is faster than the coarse ones. Secondly, as an indirect consequence of the mass transport small pores coalesce and the formation of bigger size pores occurs.

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