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Small angle neutron scattering study of pore microstructure in ceria compacts

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Abstract. Ceria powders were prepared by gel combustion process using cerium nitrate and hitherto unexplored amino acids such as aspartic acid, arginine and valine as fuels. The powders have been characterized by X-ray and laser diffraction. Cold pressed compacts of these powders have been sintered at 1250°C for 2 h. Internal pore microstructure of the sintered compacts has been investigated by small angle neutron scattering (SANS) over a scattering wave vector q range of 0.003–0.17 nm^{-1}. The SANS profiles indicate surface fractal morphology of the pore space with fractal dimensionality lying between 2.70 and 2.76.

Keywords. Ceria; sintering; pores; fractal; neutron scattering.

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1. Introduction

Ceria (CeO_2) is a technologically important material for its applications in solid-state electrochemical devices and automotive catalyst components. Microstructure of the sintered compacts of these powders plays an important role in these applications. Hence synthesis of ultra-fine ceria powder with controlled powder characteristics is of practical importance to obtain dense sintered products at a lower sintering temperature. Among the available solution chemistry routes, the combustion technique is capable of producing pure, nanocrystalline powders of oxide ceramics at comparatively low external temperatures [1]. The rapid evolution of large volume of gases during the combustion dissipates the heat of combustion and limits the rise of temperature, thus reducing the possibility of premature local partial sintering among the primary particles. The properties of the powder are primarily dependent on the flame temperature generated during the combustion, which in turn is a function of the nature of fuel and the oxidant-to-fuel ratio used [2,3]. For the present study ceria powders were synthesized using amino acids such as aspartic acid, arginine and valine as fuels. It is worth mentioning here that a new non-Euclidean geometry developed by Mandelbrot known as fractal geometry is often

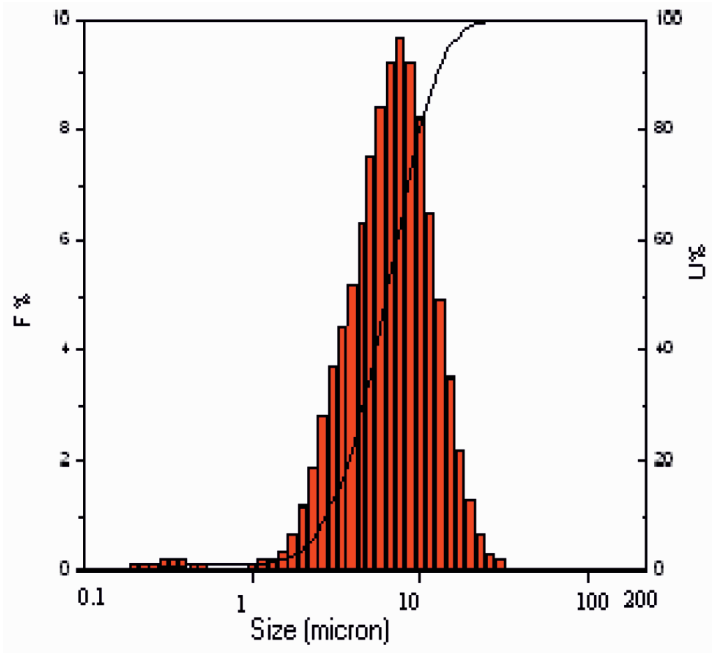

Figure 1. Representative particle (agglomerate) size distribution of CeO_2 powder (aspartic acid).

used to describe the irregular geometric structures of porous media. Interpretation of small angle X-ray/neutron scattering (SAXS/SANS) data, using fractal concept has proven to be of great value in investigating the geometric nature of porosity in porous solids [4,7–9]. Depending on the object of interest, different features of the structure can be measured: solid matrix, pore space, and the interface between them. This paper deals with SANS investigation of internal pore microstructure of sintered compacts of ceria over scattering wave vector q range of 0.003–0.17 nm^{-1}.

2. Experimental

2.1 *Powder synthesis and characterization*

Ceria powders were synthesized by the gel-combustion technique using amino acids such as aspartic acid, arginine and valine as fuels. The extent of agglomeration was studied by laser diffraction using Horiba, Model LA-500 (Japan) particle size analyzer. Figure 1 shows the representative particle size distribution of ceria powder synthesized by using aspartic acid as fuel. X-ray diffraction measurements (10–70°) on ceria powders were carried out for the crystallite size estimation, using monochromatized Cu-Kα radiation on a Philips X-ray diffractometer, Model PW 1927. Figure 2 shows the XRD pattern of ceria powders. Silicon was used as an external

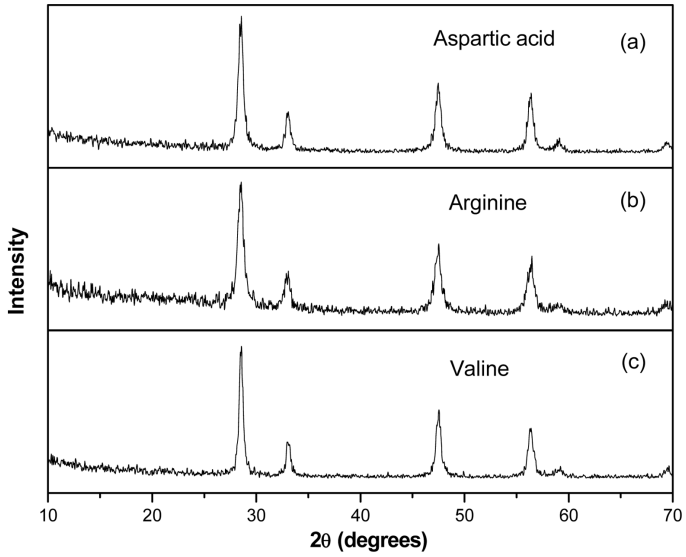

Figure 2. XRD patterns of CeO_2 powders.

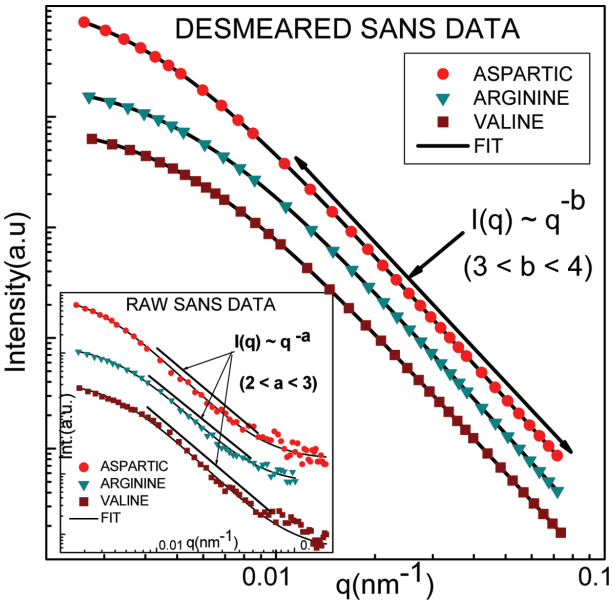

Figure 3. SANS profiles of sintered ceria pellets with fit.

standard for correction due to instrumental broadening. Using a uniaxial hydraulic press, 10 mm diameter cold-pressed compacts of ceria powders were prepared at a compaction pressure of 200 MPa and sintered at 1250°C for 2 h.

2.2 *SANS experiments*

SANS experiments on the sintered pellets were performed using a double crystal-based diffractometer (DCD) installed at Guide Tube Laboratory of Dhruva reactor at Trombay, India [5]. The instrument consists of a non-dispersive (1, −1) setting of 1 1 1 reflections from a pair of perfect silicon (Si) crystals with provision for mounting specimen between them. The scattered intensity $I(q)$ from each specimen has been recorded for several values of scattering vector q ($=4\pi\sin(\theta)/\lambda$, where 2θ is the scattering angle and the incident neutron wavelength $\lambda = 0.312$ nm) by automated rotation of the analyzer crystal in very fine angular step size of 0.0012° in the accessible q range of 0.003–0.17 nm^{-1}. For a DCD, the beam is collimated in the direction of the scattering plane of the crystals and high resolution exists only in the horizontal direction. The analyzer collects scattered neutrons over several degrees in the vertical direction and in most practical cases the primary beam can be taken as infinitely high, leading to slit-height smearing of the scattering profiles similar to that observed for a long-slit instrument. The values of the power law exponent of smeared and de-smeared profiles differ by '1'. The de-smeared SANS profile has been obtained by following the method given in ref. [6]. Background corrected de-smeared SANS profiles are shown in figure 3 and the inset shows the raw SANS profiles.

3. Results and discussion

It could be observed from figure 3 that the SANS profiles follow power-law scaling of intensity over the q regime of 0.009 nm^{-1} to 0.07 nm^{-1} and the values of the exponent b lie between 3 and 4. This behaviour is different from that normally seen in the case of scattering from regular geometric objects (rod, disc and cube) and from smooth interface. Hence scattering has been modelled using the concept of fractal geometry. It is worth mentioning here that the models based on fractal geometry have been of great value in giving simple and physically meaningful models, which explain a diverse range of data for a very wide range of porous solids [4,7–9]. In the case of a two-phase system the power-law scattering with the value of exponent lying between 3 and 4 is often attributed to scattering from fractal surfaces. A porous sintered sample can be considered as two-phase system consisting of pore space and material medium. SANS profiles have been modelled by applying fractal concept and are fitted with modified Debye–Bueche function [10], given by the expression

$$I(q, a, D_s) = I_o(1 + a^2q^2)^{-(6-D_s)/2}. \quad (1)$$

In eq. (1), I_o is the characteristic constant of the sample and is independent of q. a denotes average pore size and D_s denotes surface fractal dimension. The power-law behaviour of scattering intensity could also be attributed to a power-law distribution of pore sizes. In contrast, a non-fractal surface with regularity and smoothness would be characterized by $D_s = 2$ and would produce Porod scattering with a characteristic exponent of −4. Values of important fit parameters are tabulated in table 1.

Table 1. Values of fit parameters obtained for the specimens.

Amino acid fuel	Average pore size a (nm)	Surface fractal dim. D_s
Aspartic acid	265.0	2.72 ± 0.08
Arginine	187.0	2.70 ± 0.06
Valine	192.0	2.76 ± 0.04

4. Conclusions

SANS profiles of sintered ceria compacts prepared from the powders synthesized using different types of alpha amino acids as fuels exhibit deviation from normal scattering behaviour as observed in the case of regular geometrical shape (rod, disc and cube) particles and scattering from smooth interface. In order to interpret the observed power-law behaviour of scattering intensities fractal model was applied to SANS data of the ceria samples. The results of this preliminary investigation will be helpful for further studies on sintering behaviour of this material.

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