

Effect of porosity and pore morphology on the low-frequency dielectric response in sintered ZrO_2 –8 mol% Y_2O_3 ceramic compact

D SEN¹, T MAHATA², A K PATRA¹, S MAZUMDER¹ and B P SHARMA²

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

²Powder Metallurgy Division, Bhabha Atomic Research Centre, Vashi Complex,

New Mumbai 400 705, India

E-mail: debasis@apsara.barc.ernet.in

Abstract. Effect of porosity and pore size distribution on the low-frequency dielectric response, in the range 0.01–100 kHz, in sintered ZrO_2 –8 mol% Y_2O_3 ceramic compacts have been investigated. Small-angle neutron scattering (SANS) technique has been employed to obtain the pore characteristics like pore size distribution, specific surface area etc. It has been observed that the real and the imaginary parts of the complex dielectric permittivity, for the specimens, depend not only on the porosity but also on the pore size distribution and pore morphology significantly. Unlike normal Debye relaxation process, where the loss tangent vis-à-vis the imaginary part of the dielectric constant shows a pronounced peak, in the present case the same increases at lower frequency region and an anomalous non-Debye type relaxation process manifests.

Keywords. Porosity; pore size; small-angle neutron scattering; dielectric response.

PACS Nos 61.12.Ex; 77.22.Gm; 81.20.Ev

1. Introduction

The dielectric properties of ceramic materials are of immense technological as well as scientific interest. One of the important parameters for any dielectric material is its dielectric constant or dielectric permittivity, ϵ , which is the ability to store charge in a capacitor. In the presence of sinusoidal electric field across a capacitor with lossy dielectric, the permittivity can be expressed as $\epsilon^* = \epsilon' + i\epsilon''$. ϵ' represents the real part of the permittivity (i.e., the dielectric constant) and characterizes the material's ability to store charge and ϵ'' is the imaginary part, which is a measure of the energy dissipation in the material. Dielectric loss is generally described by the loss tangent $\tan(\delta) = \epsilon''/\epsilon'$. Extrinsic losses are associated with the imperfections, e.g. porosity, impurities, grain boundaries, micro-cracks, random crystal orientations etc. It is evident from the earlier studies [1–3] that the losses in sintered polycrystalline ceramics are strongly affected by these extrinsic factors. Few of the earlier work deals with the effect of only total porosity on the

high frequency dielectric behavior in ceramics. However, a detailed study on the pore characteristics and its effect on the low-frequency dielectric response is highly desirable.

Small-angle neutron scattering (SANS) is an important and non-destructive technique to investigate the pore characteristics in ceramics and other porous materials [4,5]. Yttria-stabilised zirconia is a potential ceramic system for various structural and functional applications. ZrO_2 -8 mol% Y_2O_3 composition has fluorite type crystal structure. Oxygen vacancies are introduced in the lattice because of aliovalent doping. Dielectric loss at low frequencies is expected due to ion migrations. The present paper deals with the investigation on pore characteristics using SANS and also the effect of the same on the low frequency (0.01–100 kHz) dielectric response in sintered ZrO_2 -8 mol% Y_2O_3 ceramic keeping porosity constant at two different porosity levels by varying sintering conditions. In the present investigation we also intend to investigate the effect of pore size and pore morphology keeping nearly constant porosity value at two porosity levels.

2. Experimental

The preparation of yttria-stabilised zirconia (fully cubic phase) through citric acid gel route has been given elsewhere [6]. For the present study, the gel has been calcined at two different temperatures, i.e. 800 and 950°C. The 800°C calcined powder has been ball-milled for 20 h to get a finer powder of median particle size 0.43 μm . The 950°C calcined powder has been hand-ground in pestle and mortar to get powder of median size 2.74 μm . Green pellets (12 mm $\phi \times$ 3 mm thick approximately) prepared by uniaxial pressing (200 MPa) were sintered at 1200 and 1400°C with different soaking times (0, 1 and 3 h). Density of the sintered pellets was determined from physical measurement. Pellets obtained from finer and coarser powder are designated as PF and PC respectively. It is seen that pellets PF-1200 (1 h) and PC-1400 (3 h) have nearly equal value of porosity ($\phi = 0.28$). Similarly, pellets PF-1200 (0 h) and PC-1400 (0 h) are of nearly same porosity values ($\phi = 0.39$). However, the pore characteristics are likely to be different from each other although the total porosity remains the same. This is because of the difference in the starting powder size and sintering conditions. The above two pairs of specimens have been taken for SANS investigation for determining their pore characteristics. SANS experiments have been performed using a double crystal based small-angle neutron scattering instrument at the Guide Tube Laboratory of Dhruva reactor at Mumbai, India [7]. The scattered intensities have been recorded as a function of wave vector transfer q . In order to correct for multiple scattering effect for the above specimens, SANS experiments have been performed for two different thicknesses of each specimen. The measured SANS profiles have been corrected for background, transmission and instrument resolution [8]. Figures 1a and 1b depict the corrected SANS profiles for the specimens. Capacitance and $\tan(\delta)$ values have been measured using GenRad RLC bridge in the frequency range 0.01 to 100 kHz. The ϵ'_r and ϵ'' values for the specimens with $\phi = 0.28$ and $\phi = 0.39$ are plotted in figures 2a and 2b respectively.

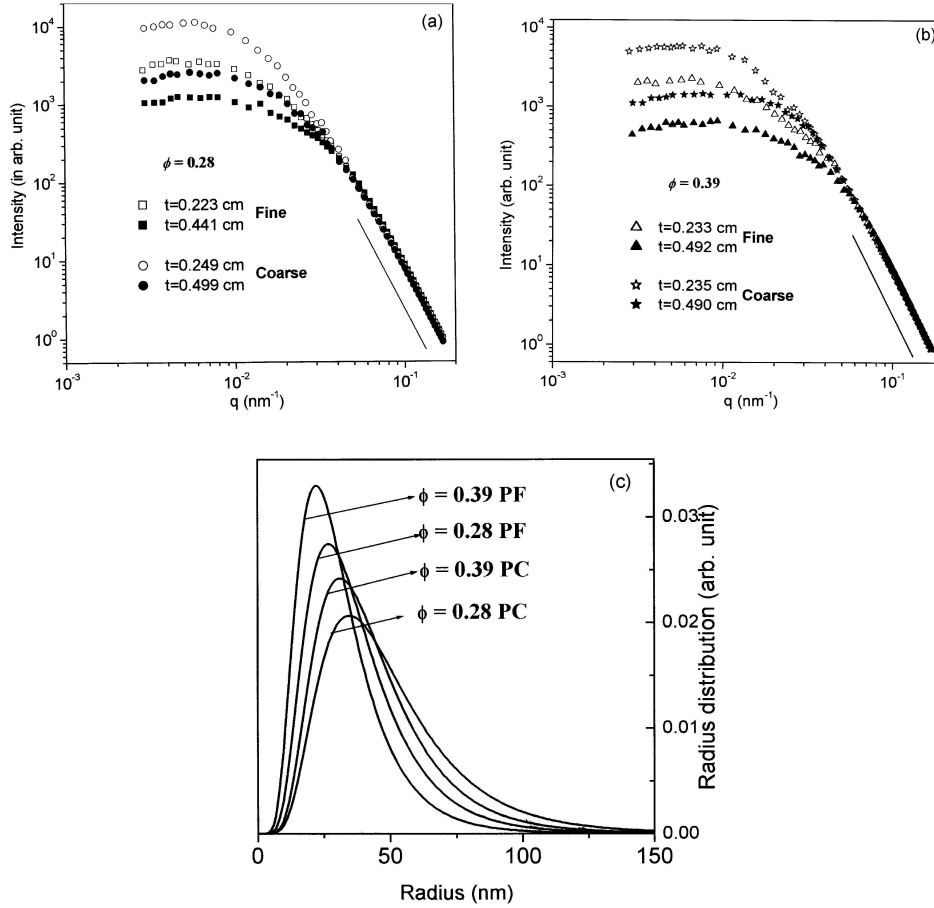


Figure 1. (a) SANS profiles from specimens with $\phi = 0.28$. (b) SANS profiles from specimens with $\phi = 0.39$. (c) Estimated pore size distributions.

3. Data analysis and discussion

In the present case, as the porosity is much less than 50%, the SANS signal is predominantly due to the pores. From figures 1a and 1b, it is discernible that the functionality of the SANS profiles for the specimens with identical porosity level (each of porosity 0.28 and 0.39 respectively) differ significantly for PF and PC specimens. In both the cases, the profiles are sharper for PC specimens. The trend is the same for both thin and thick specimens. This feature of the profiles tells, at least qualitatively at this stage, the existence of larger pores in the PC specimens. Single scattering profile [9] for each case is estimated from the SANS profiles of two different thicknesses of each specimen. The estimated single scattering profiles are analysed in the light of polydisperse spherical pore model assuming log-normal

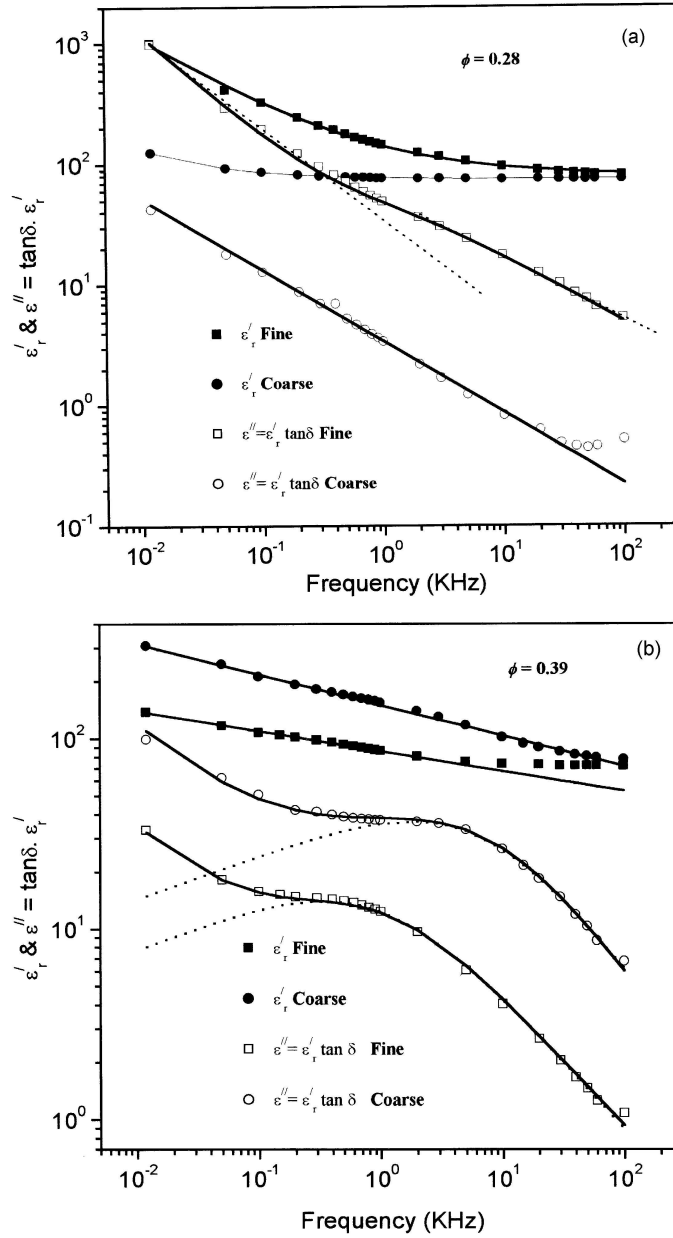


Figure 2. (a) Dielectric response for $\phi = 0.28$ specimens. (b) Dielectric response for $\phi = 0.39$ specimens.

distribution. Here it should be mentioned that all the pores in the specimens may not be exactly spherical in shape; rather they can be described by ellipsoids with modulated surface. However, in that case analysing the data will be based

Table 1. Parameters determined from the fit of the model to the estimated single scattering profiles (R_0 and σ are the parameters of log-normal distribution related to mean and width of the distribution respectively).

Specimen	R_0 (nm)	σ	$\langle R \rangle$ (nm)	Specific surface area (κ) ($\text{m}^2 \cdot \text{m}^{-3}$)
$\phi = 0.28$, fine	33.83	0.48	37.99	7.54×10^7
$\phi = 0.28$, coarse	44.30	0.49	50.10	5.58×10^7
$\phi = 0.39$, fine	28.09	0.48	31.54	9.32×10^7
$\phi = 0.39$, coarse	38.99	0.48	43.61	6.14×10^7

on minimising several nonlinear parameters and hence the question of obtaining globally minimised parameters will remain unreciprocated. The estimated pore size distributions are depicted in figure 1c. Important parameters are tabulated in table 1. It is evident that the pore size distribution for specimens ($\phi = 0.28$ and 0.39) are significantly different with respect to the PF and PC specimen. The average value of the distribution for PC specimens is significantly more than those for the PF specimens in both the cases. So, it is evident that although the porosity remained nearly the same for PF and PC specimens, the pore size distributions and average pore radii are quite different in these specimens at both the porosity levels. At this point it should also be noted that as soaking time for the specimens with $\phi = 0.39$ is negligibly small, it is expected that in this case the probability of interconnection of the pores are more than that for the specimens with $\phi = 0.28$. We have estimated the specific surface area (κ) from the extracted SSPs. It is seen that for specimens with identical porosity values, the κ value is more for the PF specimens as compared to the PC specimens.

From figures 2a and 2b which shows the dielectric response of the specimens, it is seen that at both the porosity levels, ϵ'' unlike normal Debye relaxation mechanism shows an anomalous increasing trend at low-frequency region. For specimens with $\phi = 0.39$, ϵ'' shows a nice hump between 1–10 kHz. ϵ'' in both the cases decreases with increase in frequency and becomes almost constant at higher frequency region. In the present case, the frequency dependence of ϵ'' can be explained due to the mixed contribution of ion-jump, conduction losses and interfacial effects. Interfacial effects are evident from significant variation in the response curves for PF and PC specimens where the pore morphology and pore sizes are different for the two specimens although porosity remains constant. The increase in ϵ'' at very low-frequency region is mainly because of the conduction losses and Maxwell Wagner effect. Particularly for the specimen with $\phi = 0.39$, the effect of the ion-jump losses is visible as manifested by the hump at ~ 1 kHz. However, for the specimen with $\phi = 0.28$ the effect of conduction is more pronounced over that of the ion-jump effects. This is due to the fact that for the specimen with $\phi = 0.28$, the structure is more compact and hence the probability of migration and conduction is more than that through the specimen with $\phi = 0.39$.

4. Conclusions

The low-frequency dielectric response in ZrO_2 -8 mol% Y_2O_3 is strongly affected by the porosity, the pore size distribution and pore morphology. At a given porosity level, the dielectric behavior is also influenced by the pore size distribution. SANS revealed that, at fixed porosity level, the average pore size is more and the specific surface area is less for the PC specimens indicating that the less number of pores in the same compared to PF specimen. The anomalous increasing trend of the loss part of the dielectric constant is primarily due to the conduction and the interfacial effects and is strongly influenced by the pore characteristics. The hump in the ϵ'' spectrum for the specimens with $\phi = 0.39$ is because of the loss due to the ion-jump mechanism. However, for the specimens with $\phi = 0.28$, the hump is not pronounced but only a power law type increase in the ϵ'' value is observed (particularly for the PC specimen where the number of pores is less). This is explained because of the fact that the conduction losses dominate at very low frequencies compared to that due to the ion-jump losses because of the lower porosity level, i.e., the higher compact structure which allows relatively more conduction.

Acknowledgements

We would like to thank Dr. P U Sastry of Solid State Physics Division, Bhabha Atomic Research Centre, for his kind help in the dielectric measurements.

References

- [1] S J Penn, N M Alford, A Templeton, X Wang, M Xu, M Reece and K Schrapel, *J. Am. Ceram. Soc.* **80**(7), 1885 (1997)
- [2] M Valant and D Suvorov, *Mater. Chem. Phys.* **79**, 104 (2003)
- [3] N M Alford and S J Penn, *J. Appl. Phys.* **80**(10), 5895 (1996)
- [4] D Sen, A K Patra, S Mazumder and S Ramanathan, *J. Alloys and Compounds*, **361**, 270 (2003)
- [5] D Sen, S Mazumder and S Tarafdar, *J. Mater. Sci* **37**, 941 (2002)
- [6] D Sen, T Mahata, A K Patra, S Mazumder and B P Sharma, *J. Alloys and Compounds* **364**, 304 (2004)
- [7] S Mazumder, D Sen, T Saravanan and P R Vijayaraghavan, *J. Neutron. Res.* **9**, 39 (2001)
- [8] J A Lake, *Acta Crystallogr.* **23**, 191 (1967)
- [9] S Mazumder, B Jayaswal and A Sequeira, *Physica* **B241-243**, 1222 (1998)