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Effects of sintering on microstructure and dielectric response in $YCrO_3$ nanoceramic

J BAHADUR[1,*], D SEN[1], S MAZUMDER[1], V K ASWAL[1], V BEDEKAR[2], R SHUKLA[2] and A K TYAGI[2]

[1]Solid State Physics Division; [2]Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

[*]Corresponding author. E-mail: jbahadur@barc.gov.in

Abstract. Effects of sintering on pore morphology and dielectric response have been investigated. Pore structure has been probed by small angle neutron scattering (SANS). It has been observed that the size distribution becomes less polydisperse with a slight modification in the distribution as sintering temperature is increased. Dielectric response in the frequency range 0.02–1000 kHz is significantly altered by modification of pore structure because of sintering. A transition from non-Debye type to near-Debye type response has been observed as the sintering temperature is increased.

Keywords. Nanoceramic; small angle neutron scattering; dielectric; multiple scattering; $YCrO_3$.

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1. Introduction

Multifunctional materials have been attracting a lot of attention since the last decade. In particular, biferroics which possess both ferromagnetic and ferroelectric properties are of special interest because of their potential applications in technology. Recently the rare-earth chromate, $YCrO_3$ has been found as one of the potential biferroic materials [1]. The dielectric properties of such ceramics have immense technological as well as scientific interests. The dielectric properties of materials are measured by a complex electrical permittivity ($\varepsilon^* = \varepsilon' + i\varepsilon''$). The factors, which affect the AC dielectric property are broadly classified into two categorie, namely, intrinsic and extrinsic. While the intrinsic losses depend on the crystal structure, phonon interaction etc., the extrinsic losses significantly depend on the heterogeneity of the medium such as porosity, impurities, grain boundaries, microcracks and random crystal orientation [2–4]. Electrically heterogeneous materials like a porous medium experience an interfacial polarization in the presence of electric field. In these materials the motion of charge carriers occurs relatively easier through one of the phases compared to the other one. Hence the charges are constricted at the phase boundaries. As a result, charges build up at interfaces

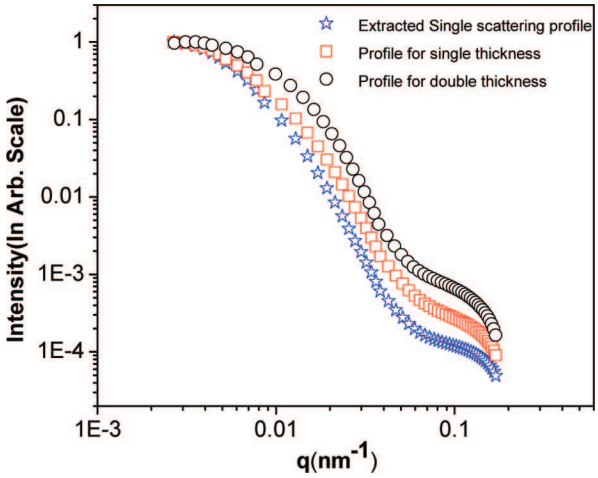

Figure 1. SANS profiles for two thicknesses and extracted single scattering profile for 1600°C sintered pellet.

and get polarized in the presence of the field. This effect often depends greatly upon the conductivities of the phases present. Sintering is a process that binds the primary particles together, i.e. it controls the microstructure from nanometer to micrometer scale and hence pore morphology and porosity get modified under sintering.

SANS is an important and non-destructive technique for probing the pore morphology in ceramics and other porous materials [5,6]. The present paper deals with SANS investigation of pore characteristics and their effect on low/intermediate frequency (0.02–1000 kHz) dielectric response of $YCrO_3$ nanoceramic for different sintering temperatures.

2. Experimental

Single phase nanocrystalline $YCrO_3$ has been prepared by combustion. The details of the sample preparation method are described elsewhere [7]. SANS experiments have been performed using a double crystal-based medium resolution small angle neutron scattering instrument (MSANS) at the Guide Tube Laboratory of the Dhruva reactor at Trombay, India [8]. The instrument consists of a non-dispersive (1,−1) setting of 1 1 1 reflections from silicon single crystals with specimen between the two crystals. The scattered intensities have been recorded as a function of wave vector transfer q ($=4\pi \sin(\theta)/\lambda$, where 2θ is the scattering angle and λ ($=0.312$ nm) is the incident neutron wavelength). SANS measurements have been carried out on pellets (sintered at 1300, 1400, 1500 and 1600°C). SANS profiles were corrected for instrumental resolution after background and transmission corrections. It is worthy to mention that due to strong scattering contrast and large inhomogeneity size, multiple scattering takes place for many porous systems. In order to correct the multiple scattering effects, SANS experiments were performed for two

Table 1. Parameters from SANS and dielectric measurements (SD → $(\langle R^2\rangle - \langle R\rangle^2)^{0.5}$).

Sintering temp.	Porosity (%)	Density (% TD)	$\langle R\rangle$ (nm)	SD (nm)	f_p (Hz)	m	n
1300°C	61	39	14.3	16.9	1.6×10^3	0.42	0.75
1400°C	59	41	8.5	9.1	0.8×10^3	0.39	0.72
1500°C	42	58	8.8	7.9	5.6×10^4	1.0	0.005
1600°C	22	78	7.6	6.5	4.0×10^4	0.99	0

different thicknesses of each specimen and single scattering profile (SSP) was extracted. Figure 1 shows the experimental SANS profile for two thicknesses and the corresponding extracted single scattering profile for 1600°C sintered pellet. It is evident from figure 1 that SSP becomes sharper to some extent after multiple scattering correction compared to experimental profiles.

Capacitance and loss factor ($\tan(\delta)$ ($=\varepsilon_r''/\ \varepsilon_r'$)) values have been measured using a RLC bridge for each specimen. Values of the relative permittivity (ε_r') at various frequencies have been calculated from the measured capacitance values by using the appropriate geometric factors. ε_r'' has been calculated by multiplying ε_r' with tan (δ). Frequency dependence of ε_r' and ε_r'' are shown in figures 2 and 3, respectively.

3. Data analysis and discussion

The scattering intensity from an ensemble of polydisperse pores is given by

$$I(q) = C \int D(R)V^2(R)P(q,R)\mathrm{d}R, \tag{1}$$

where $P(q,R)$ is the spherical form factor of a pore with radius R. The experimental SANS data (figure 4) have been fitted by assuming a log-normal size distribution of the pores. The important parameters obtained from the analysis are tabulated in table 1.

It is evident from figure 5 as well as from table 1 that the pore size distribution shifts towards the lower radius side as the sintering temperature increases. It is also observed from figure 5 that the pore size distribution becomes less polydisperse with increasing sintering temperature.

The modifications in pore size distribution also modify the dielectric response characteristics. Peak in the ε'' (figure 3) is analysed by Jonscher-type model [9,10], which is given by eq. (2)

$$\varepsilon''(f) = c_3\left[(f/f_p)^{-m} + (f/f_p)^{1-n}\right]^{-1} + c_4 f^{m1}, \tag{2}$$

where f_p characterizes the peak frequency. Here, exponents m and $1-n$ both are in the range of 0–1. The Debye response corresponds to the case where both these exponents are equal to unity, while the significant deviation from unity represents a non-Debye response. The important fitting parameters are given in table 1. From the values of m and n, a transition from non-Debye to near-Debye dielectric response

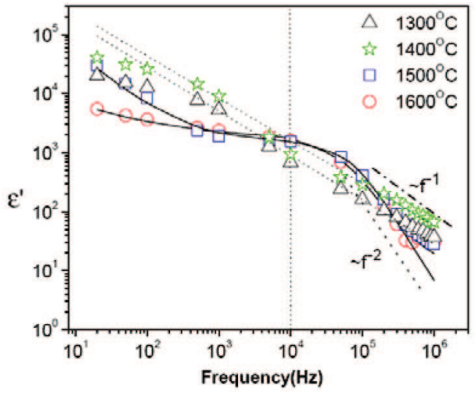

Figure 2. Frequency response ε'.

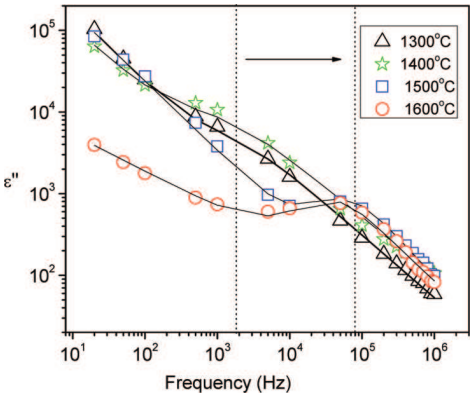

Figure 3. Frequency response ε''.

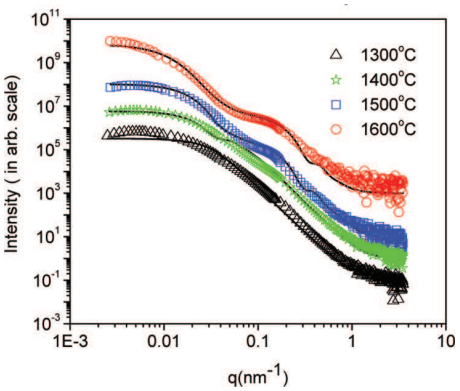

Figure 4. SANS profiles at three different sintering temperatures.

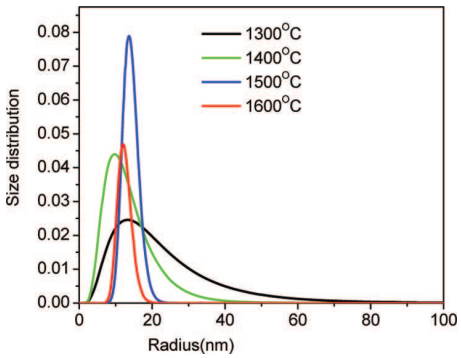

Figure 5. The pore size distribution for different sintering temperatures.

is observed as sintering temperature is increased from 1300 to 1500°C. Furthermore, this is also confirmed by the real part of frequency response also. To fit the real part of the frequency response for 1300, 1400°C for $f > f_{\mathrm{p}}$ (non-Debye response) the expression for ε' will be $\varepsilon' = cf^{n-1}$, the slope at high frequency becomes $n-1$. To fit near-Debye response for 1500, 1600°C the following model has been adopted:

$$\varepsilon' = c_1/(1 + (f/f_{\mathrm{p}})^2) + c_4 f^{-k}. \tag{3}$$

For $f > f_{\mathrm{p}}$, the slope at high frequency becomes ~ -2.

In eq. (2) the first term corresponds to dielectric response which involves a relaxation process, which occurs primarily in dipolar systems. The second term corresponds to the response from the charge carriers' movement such as conduction, hopping, jumping, diffusion etc, which is mainly responsible for the loss in the dielectric materials at lower frequencies, known as anomalous low-frequency dispersion (ALFD). As the total porosity decreases, the dielectric loss due to inhomogeneity also decreases at very low frequency regime with increase in sintering.

The peak frequency is related to the activation energy W as $f_{\mathrm{p}} \sim \exp(-W/kT)$. The activation energy depends on pores geometry [9]. As the sintering temperature is increased the specific surface gets decreased, which results in the shift in the peak frequency towards higher side [9]. The peaks at 1300 and 1400°C are not very much pronounced. This has been attributed to the fact that a significant polydispersity in the pore size remains at lower temperature. The polydispersity in the size distribution of the pores smear out the peak in the ε''. The pores at lower temperature are expected to be beyond a percolation threshold and are interconnected in a certain manner which results in a correlated dipolar system and a non-Debye type response is manifested. As the temperature is increased beyond 1500°C the pore size distribution becomes less polydisperse and the interconnection between the pores gets reduced which in turn results in non-interacting dipolar systems (uncorrelated) and a near Debye frequency response is manifested.

4. Conclusions

Reduction in polydispersity in nanocrystalline $YCrO_3$ occurs as the sintering temperature is increased. The low/intermediate frequency dielectric response shows a strong dependence on the pore characteristics. A non-Debye to near-Debye transition in frequency spectra occurs at higher sintering temperatures which can be attributed to the modifications in the pore interconnectivity *vis-à-vis* the interfacial polarization due to the pores.

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