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GRAIN AND GRAIN-BOUNDARY STUDY OF ACCEPTOR DOPED $SrTiO_3$ CERAMICS USING IMPEDANCE SPECTROSCOPY

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Abstract: Impedance spectroscopy has been used to characterize grain and grain-boundary resistivities of Ni-doped $SrTiO_3$ ceramics. The role of grain boundary was changed with Ni-doping concentration. The phenomenon was also interpreted by accounting for microstructural differences. The corresponding relaxation times were also used to confirm the interpretation of complex impedance spectra. Overlapping of Grain boundary and electrode relaxation processes can be separated above about 400^0C. Admittance spectra may be suitable to extract grain boundary impedances at relatively low temperatures. The values of grain and grain-boundary activation energy obtained by this method were relatively close to those reported earlier.

"Keywords" $SrTiO_3$; Acceptor; Impedance Spectroscopy; Grain; Grain boundary

INTRODUCTION

Ceramic oxide-based materials contain electro-active intragranular (bulk) and intergranular (grain boundary) regions, whose properties depend on the close control of micro structure- stoichiometric relationships. Grain boundaries play an important role in the electrical properties of a variety of ceramic materials and components. In a broad range of ceramics, this shows ionic conduction, mixed ionic-electronic conduction or electronic conduction, grain boundaries act as barriers for the cross transport of the charge carriers. Often, the barrier character of the grain boundary is especially pronounced in the low temperature regime. In this regime, perovskite type titanates such as $BaTiO_3$, $SrTiO_3$ etc, are employed as high permittivity dielectrics for capacitor applications. Perovskite titanates are usually doped with acceptors to prevent semi conduction in them[1].

$SrTiO_3$, a technologically highly important class of perovskite material, is used in PTC resistors, capacitors and sensors[2-3]. Acceptor, e.g. Ni-doped $SrTiO_3$ is a mixed conductor of oxygen vacancies and electron holes. The grain boundary properties of acceptor doped $SrTiO_3$ have already been investigated by impedance spectroscopy on poly-crystal and bicrystals[4], in time dependent voltage stapes measurements[5], by simulations[6], using micro-contact measurements[7] etc.

These investigations suggested that the origin of the enhanced grain boundary resistivity is due to the presence of double Schottky type space charge barrier layer at the interface. Grain boundary core is positively charged, i.e. they show donor character. The positive core is compensated by the negative charge of acceptor ions in the adjacent space charge layers while all positive mobile charge carriers (holes and oxygen vacancies) are depleted in the space charge region. Grain conductivity has been considered mainly ionic[8], at least for relatively low temperature (<400 ^{0}C) and electron holes represented the main grain boundary charge carrier in air[9]. The grain boundary conductivity was predicted to show a W-type profile for relatively high concentration of charge donors at the boundary and the activation energy of ~1.6 eV for that conductivity was also predicted[5]. They also proposed a grain boundary V-type conductivity profile for sufficiently low concentration of charged donors and/or low temperatures, with activation energy of ~1eV. The grain boundary electrical behavior was also changed by sintering, the acceptor doped ceramics in different conditions and that was interpreted by accounting for microstructural differences [10]. Thus it is evident from the literature that grain and grain boundary electrical behavior of acceptor doped $SrTiO_3$ is highly dependant on accepter concentration, type of acceptor, microstructure of the ceramics, temperatures and atmosphere, etc.

Impedance spectroscopy has been recognized as a powerful technique to distinguish the grain and grain boundary conductivity contribution of many oxide ceramics [10-12]. Traditionally, *dc* and fixed frequency *ac* measurements have been the preferred methods to characterize electro ceramics but these provide little or no information on electrical microstructure. Bauerle[11] was the first to show that *ac* methods could be used to separate the various resistances (R) and capacitance (C) values associated with the electrode reaction, grain boundary regions and grain interiors in ceramic solid electrolytes. From this study, it became apparent that *ac* techniques, particularly in the range 10^{-2} to 10^{7} Hz, now commonly referred to as impedance spectroscopy (IS) which could provide a method to probe the electrical microstructure of ceramics. In the present work we have used complex impedance spectroscopy to study the relative importance of grain and grain boundary electrical behavior in Ni- doped $SrTiO_3$ ceramics. Grain and grain boundary arc were ascribed by comparing the spectra obtained for un-doped and doped $SrTiO_3$ ceramics with varying the dopant concentration.

EXPERIMENTAL PROCEDURE

Nickel-doped (0.5 mol% and 1mol%) strontium titanate was prepared by solid-state reactions from Strontium Carbonate (S.D. Fine Chem, Mumbai), Titanium Dioxide (E. Merck India Ltd.) and Nickel Nitrate (S.D. Fine Chem, Mumbai). All the powders were having 99% purity. The powders were mixed in agate mortar using IPA up to dryness. Mixed powder was calcined at 1200^0C for 1 hr and then milled again to destroy agglomerates. The calcined powder was characterized by XRD and showed a perovskite structure without evidence of additional phases. The lattice parameter was, a=3.8995 Å, in good agreement with that of JCPDS-Card no. 35-734, (a=3.9050 Å). For electrical property measurements, the disks were pressed uniaxially at 200 Mpa with 2wt% PVA solution added as binder and that were sintered at 1300^0C for 4 hrs. Disk density, determined by water immersion methord, was ~99% of theoretical density. Microstructures were taken by optical microscope. Silver electrodes were printed on to opposite disk faces and were sintered at 700^0C, 15 minutes. Impedance measurements were carried out over the frequency range 10Hz to 13MHz and the temperature range 25 to 600^0C, using HP-4192A LF Impedance Analyzer connected with a PC.

RESULTS AND DISCUSSION

Figure 1 shows the optical micrograph of $SrTiO_3$ samples. The average grain sizes are 1.2, 3.5 and 3.8 μm respectively for undoped, 0.5 mol% and 1 mol% Ni-doped samples respectively. The samples were fired in same firing schedule and the differences in grain size may be attributed to the effect of Ni-doping. NiO may enhance grain growth at the experimental sintering temperature. It is known that overall grain boundary resistance, R_{gb} increases with the decrease in grain size due to the increase in number of boundaries per unit thickness. A typical grain-boundary thickness of nickel-doped materials was estimated of the order of 100 nm[9], which is usually much lower than the average grain size. That is why; no significant changes are expected in bulk resistance on changing the grain size. The amplitude of high frequency arc of the impedance spectra for three samples having different grain sizes does not vary significantly with increasing grain size (Table 1) and is ascribed to the bulk resistance (R_b) (Figure 2). The value of R_b is used to adjusted the scale (Z'/R_b Vs Z''/R_b) in all IS-figures, because the scales of Z* and Y* plots are dependent on temperature and normalized representation are needed to compare their trends. Low frequency arc was not found at 400^0C for the three samples, which may be due to the effect of electrode relaxation process overlapping with the grain boundary relaxation process. However, with increase in temperature (> 500^0C) the low frequency arc was found as shown in Figure 2. The low frequency arc is ascribed to R_{gb} because arc amplitude increases with decrease in temperature.

Figure 2 shows that the apparent grain boundary resistance of 0.5 mol% Ni-doped ceramics is lower than un-doped one and that may be attributed to the much higher grain size of doped sample. But, absolute R_{gb} (i.e. R_{gb} x Av. Grain size) of the sample is higher than that of un-doped one. On the contrary, 1 mol% Ni- doped sample showed higher resistance than un-doped sample and that may be explained by the formation of thicker space charge layer at the interface due to higher concentration of acceptor doping. The extracted R_{gb}, R_b and their relaxation frequencies, f_{max} for different "RC" elements at different temperatures are presented in the Table-1. For all the three samples, R_{gb} & R_b decreases and relaxation frequency increases with increase in temperature.

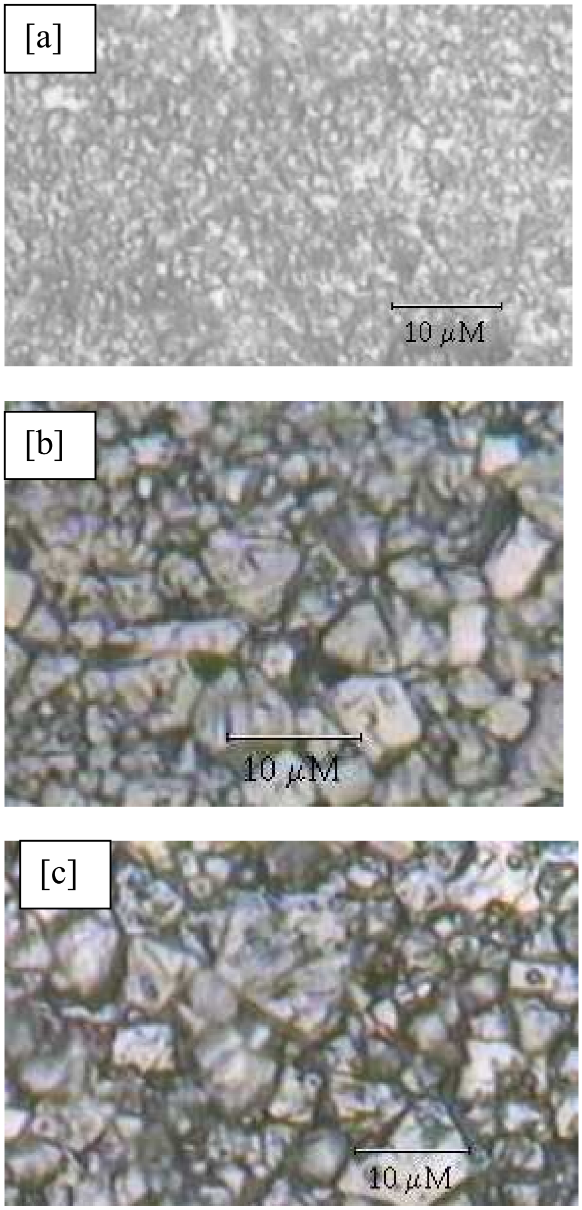

FIGURE 1 Microstructure of $SrTiO_3$ samples faired at 1300^0C/4 hours [a] un-doped, [b] 0.5 mol% Ni doped and [c] 1 mol % Ni doped.

Sample (Av. Grain Size)	Parameter	400^0C	500^0C	600^0C	Activation energy (eV)
Un-doped (1.2 µm)	R_b (kΩ)	50	5	1	0.97 (B)
	f_{max}(bulk)/kHz	27.8	310	1550	0.98 (B)
	R_{gb} (kΩ)	1600(Y*)	22.5	3.45	1.51 (GB)
0.5 mol% Ni-doped (3.5 µm)	R_b (kΩ)	50	5	1	0.96 (B)
	f_{max}(bulk)/kHz	40	400	2400	0.99 (B)
	R_{gb} (kΩ)	2400(Y*)	15	6	1.49 (GB)
1 mol% Ni-doped (3.8 µm)	R_b (kΩ)	50	5	1	0.98 (B)
	f_{max}(bulk)/kHz	45	470	2700	1.01 (B)
	R_{gb} (kΩ)	2450(Y*)	29	5.4	1.51 (GB)

TABLE 1 Fitting parameter and activation energy obtained from impedance/ admittance spectra

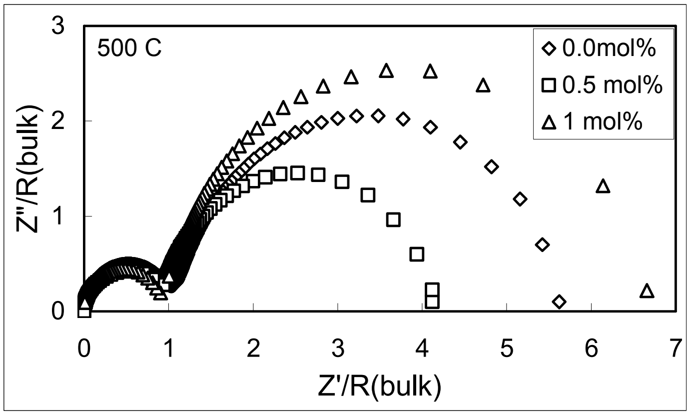

FIGURE 2 Normalized impedance spectra (Z''/R_b vs Z'/R_b) of different $SrTiO_3$ samples at 500^0C. Value of bulk resistance R_b is 5 kΩ for all three samples.

The fitted bulk resistance is multiplied with (A/L) to obtain the bulk resistivity. The results in Figure 3 show that the bulk resistivity is nearly independent of acceptor concentrations. The figure also shows the bulk resistance follow generic Arrhenius low, giving an activation energy of about ~1eV, which is close to the value reported by Waser and co-authors[5]. Also relaxation frequency (representation of relaxation times) obtained for different samples can be fitted by common temperature dependence, which again follow Arrhenius law. The relaxation time does not depend on the geometry of the sample but bulk resistance does depend on that. The values of activation energy obtained from frequency (Table-1) are also close to that obtained from resistance data.

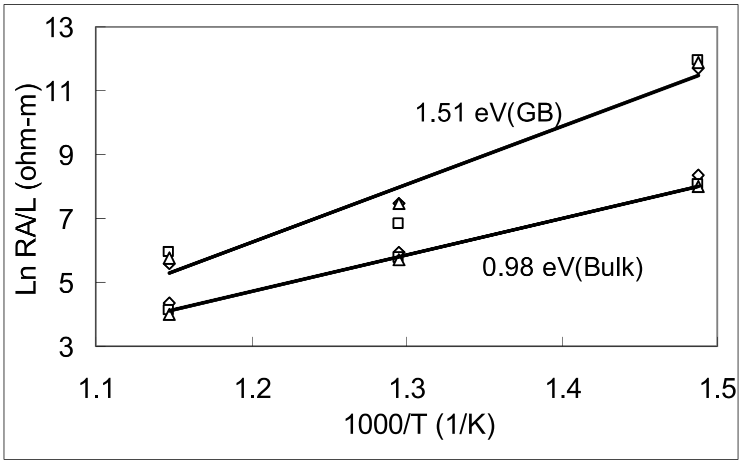

FIGURE 3 Temperature dependence of bulk and grain boundary resistivity of $SrTiO_3$ samples with; (◊) 0.0 mol% (□) 0.5 mol% and (Δ) 1.0 mol% Ni-doped.

It is already stated that low frequency arc was not found in impedance complex plane plot at 400^0C. To obtain the grain boundary resistance at 400^0C, admittance complex plain plot is used [Figure 4]. R_{gb} is extracted from the plot and presented in the table as R_{gb} (Y*). Using this R_{gb}, GB activation energy for the samples are evaluated after multiplying with (A/L). All the samples showed a typical GB activation energy of about 1.5 eV [Figure 3], which is slightly lower than the W-type conductivity profile (~1.6 eV) reported for polycrystalline Ni-doped samples [5].

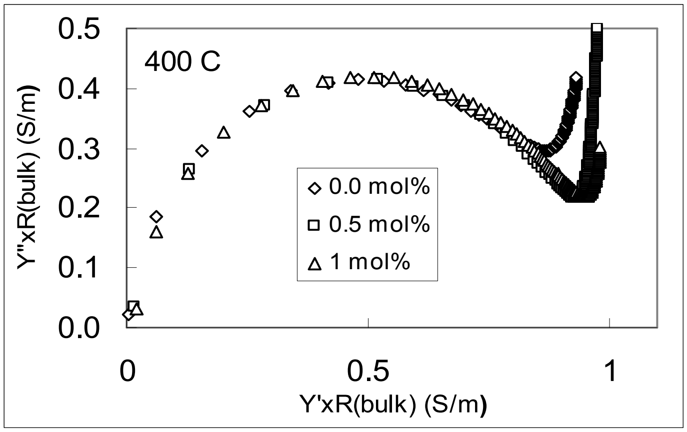

FIGURE 4 Normalized admittance spectra of representative $SrTiO_3$ samples at 400^0C

CONCLUSIONS

The average grain size of $SrTiO_3$ is changed by doping Ni into the ceramics. It may be concluded that NiO has some effect on grain growth acceleration of $SrTiO_3$ ceramics. Grain size and Ni-concentration have apparently no effect on bulk resistance. The relative values of grain-boundary resistances can be compared after accounting their average grain sizes. Grain boundary relaxation process overlaps with electrode relaxation process at relatively low temperatures. To separate them, impedance measurements above about 400^0C are required. Admittance spectra may be suitable to extract grain boundary impedances at relatively low temperature. Grain and grain-boundary Activation energy derived by this process is very much similar to those reported previously.

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