# Characterization of Ni-doped $SrTiO_3$ ceramics using impedance spectroscopy

**S K Rout, S Panigrahi & J. Bera***

Department of Physics

*Department of Ceramic Engineering

National Institute of Technology, Rourkela-769 008

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The ceramic $SrTiO_3$ (ST) with 0.2 atom % Ni doped was prepared by solid state reaction route. Average grain size of doped samples was measured and found to be 2.8 micron. The relative permittivity and dielectric loss of ST ceramics were found to increase with Ni-doping. The capacitance was measured at temperatures ranging from $400^0$ to 700 $^0$C in the frequency range 10 Hz -13MHz. The grain and grain boundaries relaxation frequencies were shifted to higher frequency with temperature. The impedance measurements were conducted at $500^0$C to separate grain and grain boundary contributions. The bulk and grain boundary resistance was evaluated from impedance complex plain plot and equivalent Resistance- Capacitance (RC) circuit is proposed to model the experimental data.

**[Keywords:** Ni doped $SrTiO_3$, Dielectric properties, Impedance spectroscopy, Grain, Grain boundary, Acceptor]

IPC Code: G01R 31/12

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## 1 Introduction

$SrTiO_3$ is used in multilayer ceramic capacitors (MLCs) and DRAM devices. Perovskite-structure titanate is frequently used as high permittivity dielectrics. MLCs types that use base metal inner electrodes (BMEs) are required to sinter under reducing atmosphere and then the titanate must be net acceptor doped to prevent semiconduction in the ceramics[1]. Acceptor doped $SrTiO_3$ (ST) is selected as our main model material because it shows a defect and crystal structure very similar to $BaTiO_3$, which still is the most important ceramic in the capacitor industry. In contrast to $BaTiO_3$, $SrTiO_3$ is not ferroelectrics over the complete temperature range of technical interest. For our purpose, this is beneficial since the ferroelectrics behaviur of $BaTiO_3$, superimpose an additional degree of complexity by significantly affecting the polarization and charge transport in the material.

Acceptor-doped strontium titanate is highly resistive at room temperature both because the acceptor dopants contributed to the suppression of the n-type conductivity, and because grain boundaries became highly resistive to the transport of positively charged carriers[2]. Waser and coauthors [3-5] analyzed the transient response of polycrystalline nickel doped strontium titanate samples. The residual conductivity in the bulk of the grains of typical acceptor-doped alkaline earth titanate ceramics has been found to be $<10^{-7}$s/m in the operating temperature regime of MLC components[6] (T<400K). The high insulation resistance of MLC components is caused mainly by the fact that grain boundaries (GBs) in the dielectric ceramic act as high resistive barriers for the cross transport of charge carriers. So, one must have proper understanding of the relative role of grain boundaries for evaluating overall behaviur of ceramic samples.

The impedance spectroscopy (IS) has been recognized as a powerful technique to distinguish the grain and grain boundary electrical contribution of many oxide ceramic materials[2,7]. Maiser and co-authors[8] found great differences between the relevant relaxation frequencies of acceptor-doped $SrTiO_3$; $f_{el}<<f_{gb}<<f_b$ . Where subscripts el, gb and b denote the electrode process, grain boundaries, and bulk respectively. Data from IS can be analysed using four different complex formalism; impedance Z*, admittance Y* or A*, permittivity **ε***, and electric modulus M*. Each consists of a real and imaginary components, for example, Z*=Z'-jZ", where Z' and Z" are the real and imaginary components of impedance, respectively and $j=\sqrt{-1}$. The four formalism are interrelated, i.e. $M^*=1/\varepsilon^*=j\omega C_0 Z^*=j\omega C_0(1/Y^*)$, where the angular frequency $\omega=2\pi f$, f is the applied frequency (in Hz) and $C_0$ is the empty cell capacitance. Data can be presented as complex plain plot, i. e. the imaginary versus real component with variable frequency or as spectroscopic plot, i.e. real and/or imaginary components as a function of log (f). All formalisms are valuable because of their different dependence on and weighting with frequency. In general, Z* and Y* are used to extract R-values where as ε* and M* are used to extract C values. An equivalent circuit consists of some combination of R and C elements connected in series and/or parallel is required to model IS data and to represent physically the various charge migration and polarization phenomena occurring in the ceramics. In the present work, a variable frequency technique of impedance spectroscopy was used to characterize Ni-doped ST ceramics. The different electro-active components were

evaluated. The most appropriate equivalent circuit can be modeled the experimental data.

## 2 Experimental procedure:

Nickel-doped (0.2 atom%) 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 $1200^0$C 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 these were sintered at $1300^0$C for 12 hr. The disk density, estimated approximately from its external dimension was ~99% of theoretical. The microstructure was taken by optical microscope (Fig. 1). Typical average grain size was 3.28 µm. The silver electrodes were printed on to opposite disk faces and sintered at $700^0$C, 15 min. The impedance measurements were carried out over range 10Hz to 13MHz using HP-4192A LF impedance analyzer, connected with a PC in the temperature range 25 - $600^0$C.

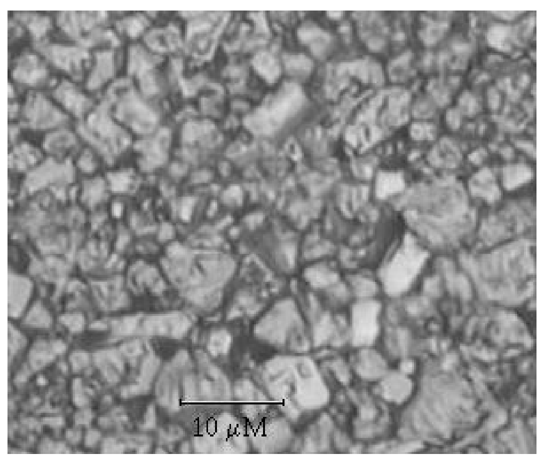

Fig. 1- Optical micrograph of Ni-doped ST ceramics.

## 3 Results and Discussion

As a first step in data analysis, capacitance and dielectric loss at 100 kHz were extracted from the impedance data and are shown in traditional fixed frequency format in Fig.2 as a function of temperature. There is a constant decrease in relative permittivity, which is the typical nature of cubic perovskite $SrTiO_3$. The rapid increase in dissipation factor D (= tanδ) after about $240^0$C is due to the increased loss with temperature. The figure also shows that Ni- doping increases the permittivity as well as dielectric loss in ST ceramics.

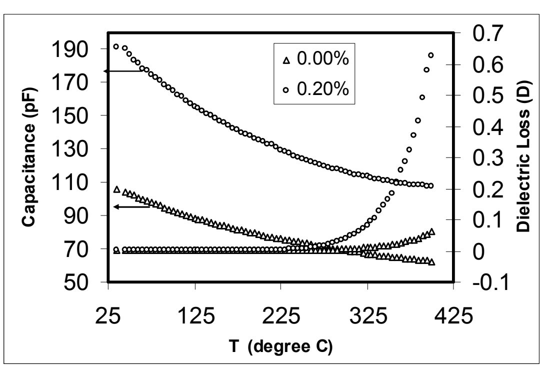


Fig.2-Temperature dependence of capacitance for Ni doped and un-doped $SrTiO_3$ at 100 kHz.

In order to carry out a more thorough analysis of permittivity and their temperature dependence, it is of course necessary to separate the contributions of the various grain and grain boundary components. The importance of making this separation is seen from Fig.3, in which capacitance data obtained by processing the experimental impedance data at several temperatures are shown as a function of frequency. The data generally showed two plateaus separated by dispersion over a range of intermediate frequencies[9]. In the present case, only dispersion and high frequency platue is found. With increasing temperature, the spectrum is displaced towards higher frequencies. Both the high frequency plateau and dispersion move to higher frequency with increasing temperature as

$C_b$ (bulk capacitance) decreases with temperature and $R_b$ (bulk resistance) also decreases with temperature. The increase in capacitance in the high frequency zone is due to the inductive effect.

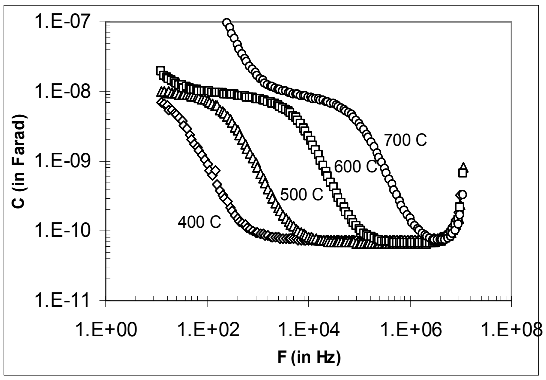


Fig.3 -Frequency dependence of capacitance for Ni-doped ST

At low frequency plateau ε is given by $\varepsilon' = \varepsilon_{gb}$, high frequency plateau permittivity ($\varepsilon_h$), is $\varepsilon_h = (\varepsilon_b^{-1}+\varepsilon_{gb}^{-1})^{-1}$. However $\varepsilon_b$, and $\varepsilon_{gb}$ cannot be evaluated, as low frequency plateau is not well defined. For a more complete analysis complex plain plots were used.

As proposed by A R West and co-author[9] admittance complex plain plot is more suitable for finding the low frequency data, we have plotted the same complex plain plot and presented in Fig. 4. Here the surface layer response is not so clear to draw the RC equivalent circuit but it is sufficient to find the activation energy. Hence the activation energy was calculated and found to be 0.98eV and 1.48eV for grain and grain boundary respectively. The same procedure for calculation of activation energy is followed as by other researchers [10-14]. As the complex plain plots at other temperature are not shown in the paper, directly activation energies were presented.

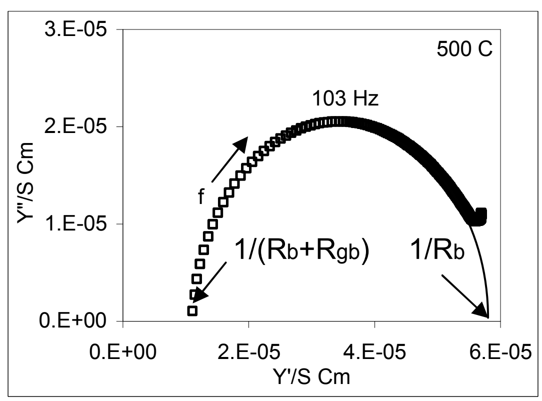


Fig.4- Complex admittance plain plot of Ni-doped $SrTiO_3$ at $500^0C$

In Fig.4 there is only low frequency arc and the two intercept Y' axis to give $1/R_b$ and $1/(R_b+R_{gb})$ as $\sim5.85X10^{-5}$ Ω and $\sim1.11X10^{-5}$ respectively. Then $R_b$ and $R_{gb}$ are calculated to be $\sim1.70X10^{4}$Ω and $\sim7.31X10^{4}$Ω respectively. To draw the RC equivalent circuit complex impedance plain plot is consulted and represented as in the Fig.-5.

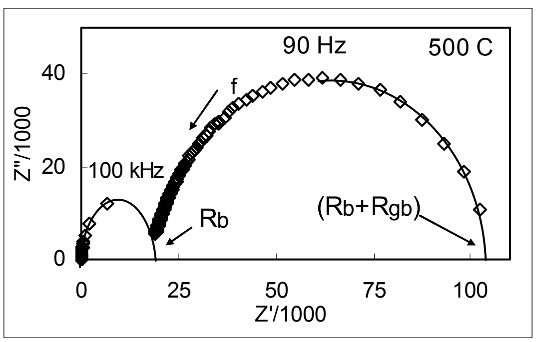


Fig. 5-Complex impedance plane plot of Ni-doped $SrTiO_3$ at $500^0$C

It shows two semicircle (arc), representing two RC element. The high frequency arc which corresponds to $R_bC_b$ response and low frequency arc corresponding to $R_{gb}C_{gb}$ response. The grain and grain boundary relaxation frequencies are 90 Hz and 100 kHz respectively. $R_b$ and $R_{gb}$ were extracted from the intercepts on Z' axis and then $C_b$ and $C_{gb}$ are calculated using the formula, ωRC =1, where ω= $2\pi f_{max}$. It is found that $C_b$ and $C_{gb}$ are 88.436pF and 20.33nF respectively. Taking the average of these extracted and evaluated data from different complex plain plot, the equivalent RC circuit can easily be drawm. Again the activation energy was calculated and found to be 0.99 and 1.50eV for grain and grain boundary respectively which are slightly lower than the W- type conductivity profile (~1.6eV) reported for polycrystalline Ni doped samples[4]. Here the activation energy is more or less the same as observed from admittance complex plain plot.

**4 Conclusions**

It is well known that acceptor doped $SrTiO_3$ has positively charged GB interface, which gives rise to an electrostatic repulsion of positively charged mobile oxygen vacancies at both side of the boundary[3]. In Ni- doped $SrTiO_3$ grain boundary relaxation process overlaps with grain and electrode relaxation process at relatively low temperatures. To separate them, impedance measurements above about $400^0C$ are required. Using Ni- doped $SrTiO_3$ as a model system for acceptor doped perovskite structured ceramics, grain and grain boundary impedances were evaluated by impedance spectroscopy. Based on the experimental data the following can be concluded:

(1) Electrical conductivity follows Arrhenius law, (2) Ni- doping increases the permittivity as well as dielectric loss in ST ceramics, (3) Grain and grain boundary capacitance and resistances can be evaluated from impedance and admittance plain plot. (4) Microstructure plays an important role in dielectric behavior of ST ceramics.

## 5 References:


1 Hagemann H J, Hennings D, & Wernicke R, *Philips Tech Rev*, **41**(1983/84) 89.

2 Jurado J R, Colomer M T & Frade J R, *J.Am.Ceram Soc*, **83** (2000) 2715.

3 Vollmann M & Waser R, *J Am Ceram Soc*, **77** (1994) 235.

4 Vollmann M, Hagenbeck R & Waser R, *J Am Ceram Soc*, **80** (1997) 2301.

5 Vollmann M & Waser R, *J Electroceramics*, **1** (1997) 51.

6 Waser R *J Am Ceram Soc*, **74** (1991)1934.

7 Rodewald S, Fleig J & Maier J, *J Am Ceram Soc*, **84** (2001)521.

8 Denk I, Claus J, Maier J, *J Electrochem Soc*, **145** (1997) 3526.

9 Hirose N & West *A R J Am Ceram Soc*, 79 (1996) 1633.

10 Abrantes J C C, Labrincha J A, & Frade J R, *Material Research Bulletin*. 35 (2000) 965

11 Abrantes J C C, Labrincha J A, & Frade J R *J European Ceramic Society* 20 (2000) 1603

12 Abrantes J C C, Labrincha J A, .Frade J R, Feighery A, Ferreira A A L, *J Am Ceram Soc*, 85 (2002) 2745.

13 Rout S K, Bera J, Ferroelectrics, (In press).

14 Rout S K, Bera J, Indian J of Physics, 78 (8) (2004) 819.