Dielectric properties of acceptor doped $SrTiO_3$ ceramics

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Abstract: 0.5 atom % Ni-doped $SrTiO_3$ was prepared by solid-state reaction route. Average grain sizes of un-doped and doped samples were 1.3 and 4.1 micron respectively. Relative permittivity of ST ceramics was found to increase with Ni-doping. Capacitance was measured at temperatures ranging from 400^0 to 700^0C in the frequency range 10 Hz to 13 MHz. Grain and grain boundaries relaxation frequencies were shifted to higher frequency with temperature. Impedance measurements were conducted at 400^0C to separate grain and grain-boundary contributions. Bulk and grain-boundary resistance were evaluated from impedance complex plain plot. Bulk resistance of doped and un-doped ST ceramics was more or less same. Single grain boundary resistance of doped sample was higher than un-doped one, indicating GB resistance increases with acceptor doping.

Key Words: Ni doped $SrTiO_3$, Dielectric properties, Impedance spectroscopy, Grain, Grain-boundary, and Acceptor.

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1. Introduction

Alkaline-earth titanates like $SrTiO_3$ (ST) are materials widely used in[1] microelectronic devices due to its excellent dielectric properties and high thermal stability. Important applications of $SrTiO_3$ are, as a substrates for the heteroepitaxial growth of high T_c superconductors [1-2], in multi-layer capacitors [3] and DRAM devices [4] etc. For most of the above applications, the titanate must be net acceptor doped to prevent semi-conduction in the ceramics. 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. Often, under high temperatures and high voltage fields, these resistive grain boundary barriers are reduced and that give rise to a substantially field-enhanced leakage currents through the components. That is why a detailed dielectric studies, especially at GB barrier interface is important for the perovksite-type titanates.

Mainly Ni, Fe, Al etc [5-10] are used as acceptor in $SrTiO_3$ ceramics. Acceptor-doped strontium titanate is highly resistive at room temperature both because the acceptor dopants contribute to the suppression of the n-type conductivity and because grain boundaries became highly resistive to the transport of the transient charged carriers [9]. It has positively charged GB interface, which gives rise to an electrostatic repulsion to positively charged mobile oxygen vacancies at both sides of the boundaries [6]. High resistance of gain boundary is due to the presence of double Schottky-type depletion space charge layer in the ceramics. Waser and coauthors [5,6,8], investigated the impedance contribution of grain boundaries

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in polycrystalline nickel doped strontium titanate, under the time and frequency domain. They suggested that the grain conductivity might be mainly ionic, at least for relatively low temperatures (T < 633 K). The grain boundary conductivity tented to increase with oxygen partial pressure [8], which indicated that electron holes were the main grain boundary charge carriers. Hebb-Wagner polarization technique was applied by J. Maier and co-authors [11] to separate electronic and ionic partial conductivities in the grain boundary of Fe-doped $SrTiO_3$. Based on their studies, they concluded that the over all grain boundaries were almost purely electronically conductive.

Relative resistances of bulk and GBs in Fe-doped $SrTiO_3$ were adjusted by changing the firing temperature and/or time [9]. The changes were interpreted by accounting for micro structural changes in the ceramics. Impedance spectroscopy (IS) has been recognized as a powerful technique to distinguish the grain and grain boundary electrical contribution of many oxide ceramic materials [9,10]. In the present work, variable frequency technique of impedance spectroscopy was used to characterize Ni-doped ST ceramics. Variations of electrical properties with acceptor doping, as well as with its microstructure, were investigated. This type of study (microstructure dependent electrical properties) on Ni-doped ST ceramics was not reported earlier in the literature.

2. Experimental

Acceptor doped (Ni~0.5 atom%) and un-doped 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=3.9050Å).

For electrical property measurements, the disks were pressed uniaxially at 200 Mpa with 2wt% PVA added as binder and that were sintered at 1300^0C for 12 hrs. Disk density, estimated approximately from its external dimension, was ~99%. Microstructures were taken by optical microscope. Silver electrodes were printed on to opposite disk faces and were sintered at 700^0C for 15 minutes. Capacitance was measured in the range from 400^0C to 700^0C at 100^0 interval. Impedance measurements were carried out at 400^0C over range 10Hz to 13MHz using HP-4192A LF Impedance Analyzer, connected with a PC.

3. Results and Discussion

Fig. 1 shows the micrograph of ST ceramics. Undoped ceramics (Fig.1(a)) has average grain size ~1.3 micron and Ni-doped sample (Fig.1(b)) has ~4.1 micron. Both the samples were sintered at same temperature and schedule. So, Ni-doping may be considered to produce the grain growth in ST-Ceramics.

Permittivity and dielectric loss at 100 kHz are shown in Fig.2 as a function of temperature. There is a constant decrease in relative permittivity with temperature, which is the typical nature of cubic perovskite $SrTiO_3$. Permittivity of $SrTiO_3$ is found to increase with Ni-addition, which may be due to the increase in average grain size of the ceramics as well as increase in space charge polarization. Dielectric loss of both the samples are more or less stable in the temperature range shown in the figure.

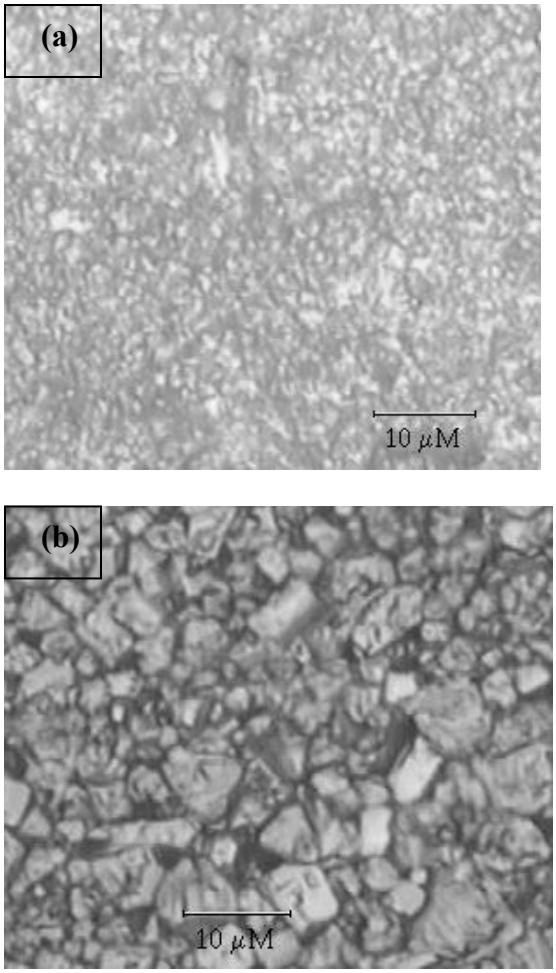

Figure 1. Micrograph of (a) un-doped and (b) 0.5 atom% Ni-doped $SrTiO_3$.

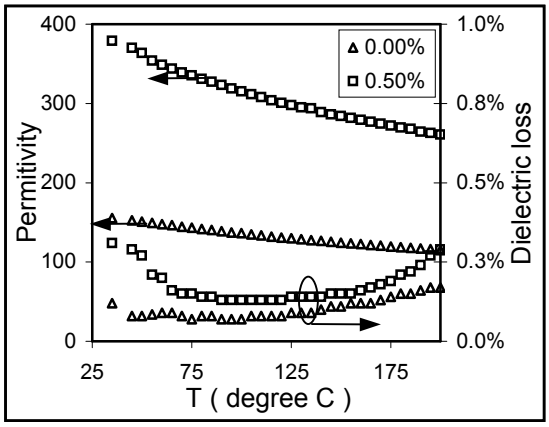

Figure 2. Temperature dependence of permittivity and Loss of 0.5 atom % Ni doped and un-doped $SrTiO_3$ at 100 kHz.

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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 grain and grain boundary components. The importance of making this separation is seen from Fig.3, in which the capacitance data at several temperatures are shown as a function of frequency for doped ST ceramics. The data shows two plateaus separated by dispersion over a range of intermediate frequencies.

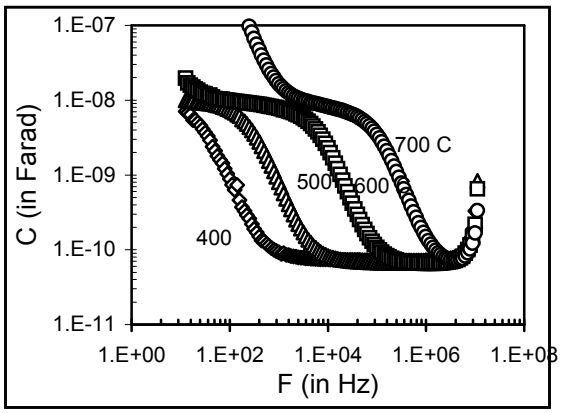

Figure 3. Frequency dependence of capacitance as a function of temperature for doped ST ceramics.

With increasing temperature, the spectrum is displaced towards higher frequencies. Both the plateaus and the dispersion move to higher frequency with temperature, as C_b (bulk Capacitance) and R_b (bulk resistance) decreases with temperature. Increases in capacitance in the high frequency zone are due to the inductive effect. Low frequency plateau is dominated by grain boundaries behavior and high frequency plateau by bulk behavior. Relative permittivity at low and high frequency may be represented by, $\varepsilon'_{low}=\varepsilon_{gb}$, and $\varepsilon'_{high}=(\varepsilon_b^{-1}+\varepsilon_{gb}^{-1})^{-1}$, respectively [12]. But, in the present case, ε_{gb} can't be evaluated, as low frequency plateau is not well defined.

For a more complete analysis of such permittivity data, impedance complex plain plot is required. Fig.4 shows the normalized Z* complex plain plot for un-doped $SrTiO_3$ at 400^0C. The value of R_b is used to adjust the scale (Z'/R_b Vs Z"/R_b) as per reference [9]. It (Fig.4) has two semicircle (arc), representing two RC elements. High frequency arc corresponds to R_bC_b response and Low frequency arc corresponds to $R_{gb}C_{gb}$ response. Grain and grain-boundary relaxation frequencies are at 70 kHz and 28 Hz respectively. R_b =2.5x10^4 Ω and R_{gb}= 11.75x10^4 Ω, are extracted from the real axis intercepts. To compare grain boundary resistivities of samples having different L/A ratio (L= thickness and A=Area) and average grain size d_g, normalization with respect to the same is required. (Ad_g/L) is to be multiplied with the extracted R_{gb} values to adjust the number of grain boundaries across the sample. Since, A/L is same for two samples, it is neglected. Hence, the corrected grain boundary resistivity, R_{gb} is ($R_{gb}d_g$) = 11.75x10^4Ωx1.3x10^{-6}m = 15.275x10^{-2}Ωm.

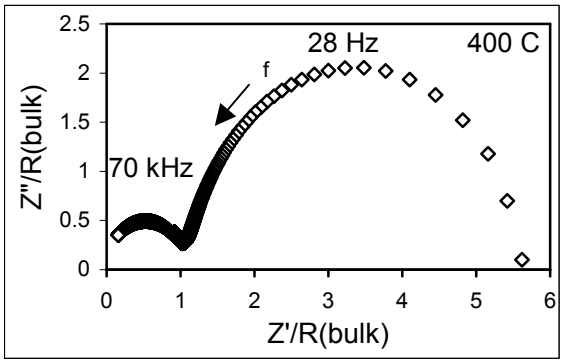

Figure 4. Normalized Z* complex plain plot of un-doped $SrTiO_3$ at 400^0C, having R_b= 2.5x10^4 Ω.

Fig.5 shows normalized Z* plot for Ni-doped sample at 400^0C. It has also two arc, having f_{bulk}=100kHz, f_{gb}=90Hz, R_b=2.1x10^4 Ω and R_{gb}= 8.61x10^4 Ω. Corresponding corrected grain boundary resistivity, R_{gb} (=$R_{gb}d_g$)=8.61x10^4Ωx4.1x10^{-6} m = 35.301x10^{-2}Ωm. R_b of the doped and undoped ceramics is more or less same, which is due to their same type of bulk grain behavior. A slight decrease in R_b for doped sample may be due to the formation of more positively charged mobile oxygen vacancies in the ceramics. Low frequency arc amplitude of un-doped ST (Fig.4) is apparently higher than that of doped one (Fig.5) due to the small grain size of un-doped sample. It is well known that R_{gb} increases with the decrease in grain size due to the increase in number of boundaries per unit thickness [9]. Ni doping should produce more resistive grain boundary in the doped samples. Actual GB resistivity of doped sample is found higher (35.301x10^{-2}Ωm) than undoped one (15.275x10^{-2}Ωm), after considering grain size contributions. So to compare this type of data, either all the samples should have same range of average grain sizes, or grain size correction should be incorporated. It can be concluded that grain size distribution plays an important role in electrical behavior of acceptor-doped titanate ceramics. Thus to get higher GB resistance, fine-grained (low average grain size) ST ceramics are desirable.

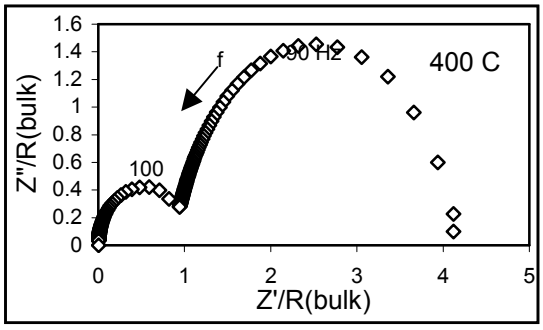

Figure 5. Normalized Z* complex plain plot 0.5 atom% Ni-doped $SrTiO_3$ at 400^0C, having R_b= 2.1x10^4 Ω.

4. Conclusion

Using Nickel-doped $SrTiO_3$ as a model system for accepter doped perovskite-structured ceramics, grain and grain boundary impedances were evaluated by

impedance spectroscopy and effect of temperature on permittivity, acceptor addition, and microstructures were studied. Based on the experimental data the following can be concluded:

1. Ni-doping acts as grain growth accelerator in titanate ceramics.
2. Ni-doping increases the permittivity and GB-Resistivity in ST ceramics.
3. Grain and grain boundary electrical behavior is temperature dependent at least above 400 ^{0}C.
4. Bulk and GB resistivity changes with acceptor doping and GB resistivity is grain size dependent.
5. Fine-grained ST ceramics are desirable for higher GB resistivity.

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