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Electrical properties of Sn doped $SrTiO_3$

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Abstract. The crystal structure and electrical properties of $SrTiO_3$ with addition of 50 mol% SnO_2 was studied. Samples were prepared using conventional solid-state reaction route. The results indicate that Sn doped $SrTiO_3$ was single phase with cubic phase and space group Pm-3m after final sintering temparture at 1400ºC. Two semicircular arcs clearly observed in Z” versus Z’ plots for $SrTi_{0.5}Sn_{0.5}O_3$ semicircles associated with bulk relaxation processes and grain boundary effect. The heterogeneity of sample was observed form Z’ and M” spectroscopic plot. The highest dielectric constant is observed at much higher temperature which nearly 2000 at low frequency measurement.

Keyword: $SrTiO_3$, $SrSnO_3$, dielectric, Impedance Spectroscopy

INTRODUCTION

Strontium titanate is a material of considerable interest with possible application such as capacitor, dielectric resonator antenna [1-4], use as the anodes in fuell cell [5], as oxygen sensors, in photo-catalysis to hydrolyse water and use as a substrate for growing YBCO superconductors [6]. For microelectronic industry, $SrTiO_3$ was reported to be useful materials for varistors [6] and reversible electronic switching for Resistive Random Access Memory (RRAM)[7]. Strontium titanate without doping usually exists in cubic, tetragonal, orthorhombic and rhombohedral depend upon temperatures. The modifications of various properties of $SrTiO_3$ materials can be achieved by doping in one or both cationic sublattices with various cations either similar in charge or size known as aliovalent or isovalent dopant. The substitution of Sn ions into the A sites of the perovskite lattice has recently been a subject of intensive research, because this is a promising approach for the fabrication of Pb-free ferroelectric materials [8] However, the synthesis of ferroelectric ABO3 substituted Sn ions for the A sites was found to be difficult in experimental studies [9]. Recently, we succeeded in obtaining ferroelectric perovskites in which Sn ions were doped into the A sites. A lot of papers have been devoted to studies on the defects and optical properties of Sn doped $SrTiO_3$. In this paper, we will report the effect of Sn by doping into $SrTiO_3$ in term of electrical properties as Sn was reported to exhibit a giant permittivity in other related perovskites materials [10].

EXPERIMENTAL PROCEDURE

$SrTi_{0.5}Sn_{0.5}O_3$ was prepared by conventional solid state reaction of strontium carbonate ($SrCO_3$) (99.9% Sigma Aldrich), titanium oxide (TiO_2) (99% Sigma Aldrich) and stanum oxide (SnO_2) (99% Sigma Aldrich). The compounds were mixed in an agate mortar with addition of acetone to obtain a homogeneous mixture. Powders were pressed into pellets of diameter 13mm. Pellets were heated at 1000ºC for 6h and continue to heat at 1400ºC with heating rate 5ºC/m in the muffle furnace. Pellet was then sintered for 1500ºC for 5h in air followed by characterization using X-ray

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Diffraction and Impedance measurement. X-ray Diffraction (XRD) was conducted at room temperature to determine the crystalline structure of all samples by using Bruker D2 Phaser benchtop X-ray diffractometer equipped with LYNXEYE 1Ddetector with Cu–K_α radiation in a 2θ range from 10^o to 80^o. The electrical properties of ceramics such as dielectric constant (ε_r) and dielectric loss (tan δ) were studied by using HIOKI 3522-50 LCR HiTESTER. For electrical measurement, sintered pellets were coated with silver paste as an electrode. Samples were measured over the frequency range of 10 Hz – 100 kHz with different temperature between 30^oC and 300^oC.

RESULT AND DISCUSSION

Figure 1 shows the comparison of XRD patterns for $SrTi_{0.5}Sn_{0.5}O_3$ that was heated at 1400 ˚C in air. The reflections of patterns were similar to the High Score Plus database referring to PDF card 01-074-1298. The patterns were taken between 2θ = 10˚ to 90˚. It can be observed that 8 intensity peak was found in this sample. Additionally, the highest intensity of the sample was determined at 2θ between 31˚ and 32˚ (110). Reflection of peak become sharper and well defined after peak was heated at 1400 ˚C for 12 hours. The lattice parameter of the element is a = 4.0254 (Å), b = 4.0254 (Å) and c = 4.0254 (Å) at 1400 ˚C.

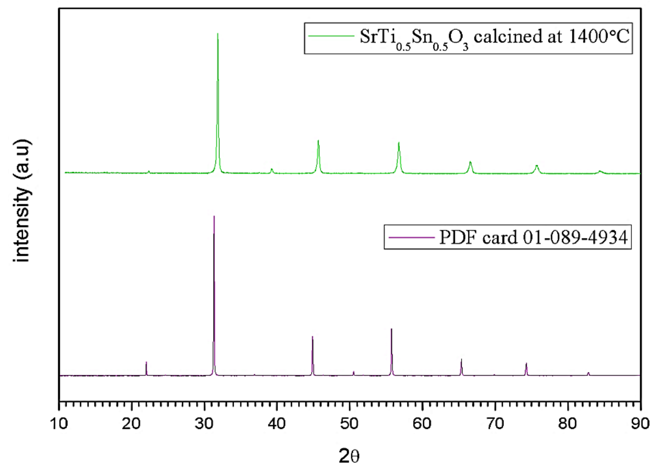

FIGURE 1. The comparison XRD pattern for $SrTi_{0.5}Sn_{0.5}O_3$ heated in air at 1400 ˚C and PDF card 01-074-1298.

The impedance plots, Z” versus Z’ for $SrTi_{0.5}Sn_{0.5}O_3$ at selected temperature of 270 ˚C are shown in Fig. 2. The plot was measured at difference temperature in range between 30 ˚C and 300 ˚C. The impedance plots Z” versus Z’ for $SrTi_{0.5}Sn_{0.5}O_3$ were measured at higher temperature range starting from 250 ˚C to 300 ˚C. At temperature 270 ˚C, two semicircular arc are present in Z” versus Z’ plot for $SrTi_{0.5}Sn_{0.5}O_3$. It can be observed that the broad arc is shown at much lower frequency. Meanwhile, at higher frequency region, the small semicircular arc was clearly observed. Regarding to the impedance theory was reported in literature, semicircles associated with bulk relaxation processes, grain boundary region and electrode respectively in the plots Z” versus Z’ of many conducting materials [11–12].

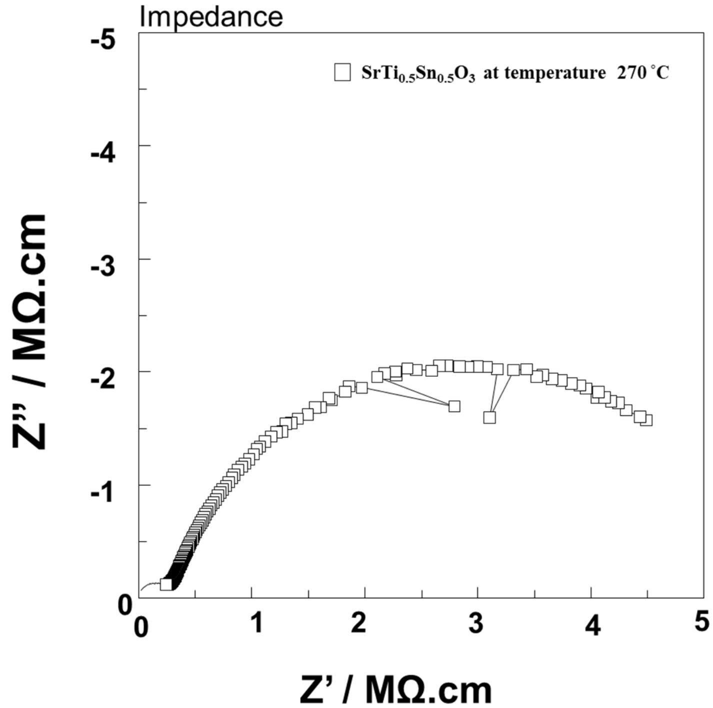

FIGURE 2. Impedance plots, Z" versus Z' for (a) $SrTi_{0.5}Sn_{0.5}O_3$ $SrSnO_3$ measured at 270°C

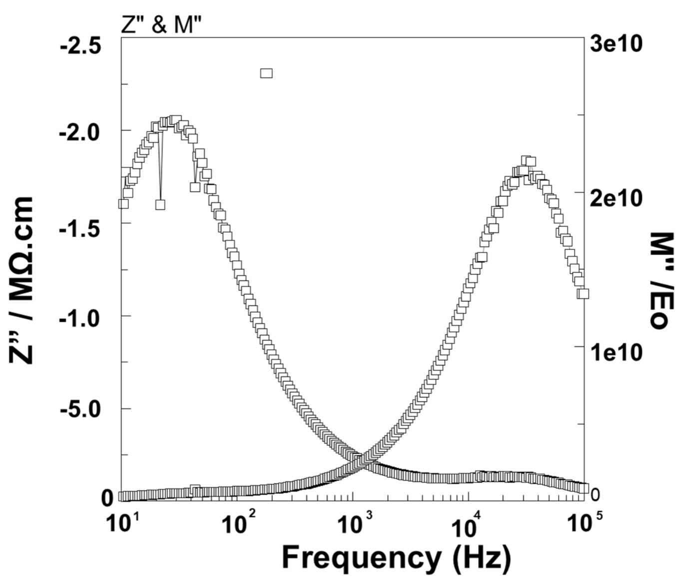

FIGURE 3. Cole-cole plot, Z″/M″ spectroscopic plots at temperature 270 ˚C

Figure 3 shows the cole-cole plot, Z″/M″ spectroscopic plots at temperature 270 ˚C. From the observation of Z"/M" spectroscopic plots, it can be conclude that low frequencies dominated the Z″ range and elevated frequencies dominated the M″ range. This kind of behavior indicating a microstructure that is inhomogeneous. Furthermore, M″ spectrum is associated with the bulk response of a sample when these happen at significantly greater frequencies and are associated with the lowest capacitance in equivalent circuit.

Figure 4 shows dielectric constant value versus temperature of $SrTi_{0.5}Sn_{0.5}O_3$. The dielectric constant values were measured between frequency 10^1 Hz and 10^5 Hz at the temperature range of 30 ˚C to 300 ˚C. At frequency 100 kHz the dielectric constant value remain constant until 300 ˚C. The highest values of the dielectric constant were record at frequency 10 Hz ($\varepsilon\sim 2000$) followed by 100 Hz ($\varepsilon\sim 1400$) and 1 kHz ($\varepsilon\sim 500$) in between temperature range of 200 ˚C – 300 ˚C. The dielectric constant is increase as temperature increase is significant with typical ceramics properties. Sn doped SrTiO3 has a good electrical properties for low frequency application.

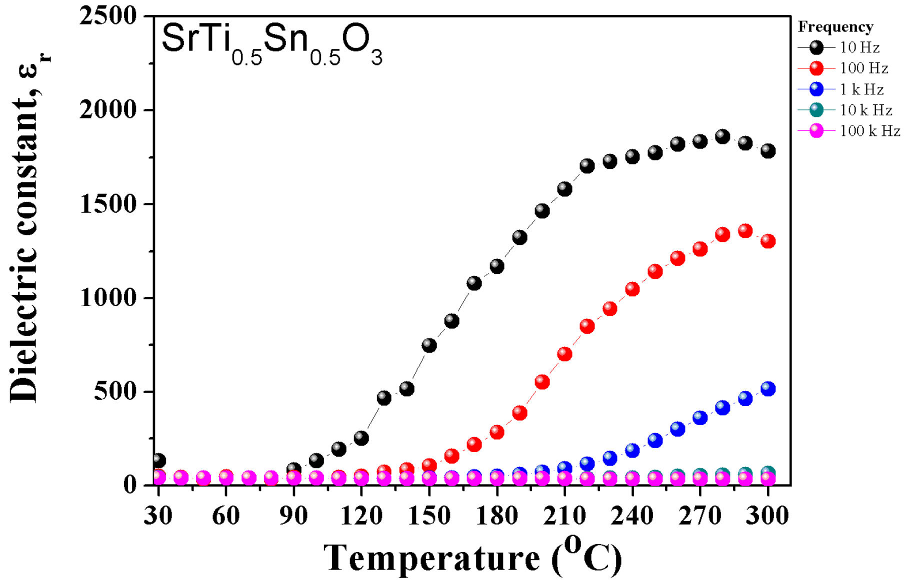

FIGURE 4. Dielectric constant of $SrTi_{0.5}Sn_{0.5}O_3$ as a function of temperature.

Figure 5 shows capacitance value versus frequency of $SrTi_{0.5}Sn_{0.5}O_3$ from temperature 120 ˚C to 300 ˚C at frequency range 10^1 Hz to 10^5 Hz. The values also were analyzed and it reveals that there is variation in capacitance values of $SrTi_{0.5}Sn_{0.5}O_3$ sample. $SrTi_{0.5}Sn_{0.5}O_3$ sample shows frequency dependent by temperatures. As a result, the capacitance value for $SrTi_{0.5}Sn_{0.5}O_3$ sample record the highest value at initial frequency for all temperature and also decrease when frequency were increase. The capacitance value was obtained for $SrTi_{0.5}Sn_{0.5}O_3$ around 10^{-9} to 10^{-11} F, which the maximum value of capacitance was found at temperature 300 ˚C around 10^{-9} F. The capacitance result shows it electrical properties could be divided into two region or component. Firstly, the capacitance value were found in the range between 10^{-9} F that indicate ceramic microstructure occurs in practice and found that grain boundary capacitance lies at the range 10^{-9} to 10^{-11} F [13]. Another region of capacitance is observed in range between 10^{-10} and 10^{-11} F which also indicate the grain boundary affect the capacitance value. The capacitance values were decreased when frequency start exceed about 10^2 Hz. In addition, it can be observed the capacitance graph shows the constant value when it exceed frequency about 10^4 at all temperature. These high capacitance values are attributed to the presence and mobility of oxygen vacancies in the lightly reduced sample which are blocked at the electrodes. The smaller capacitance values in air may indicate that the concentration of mobile oxygen vacancies is smaller [14].

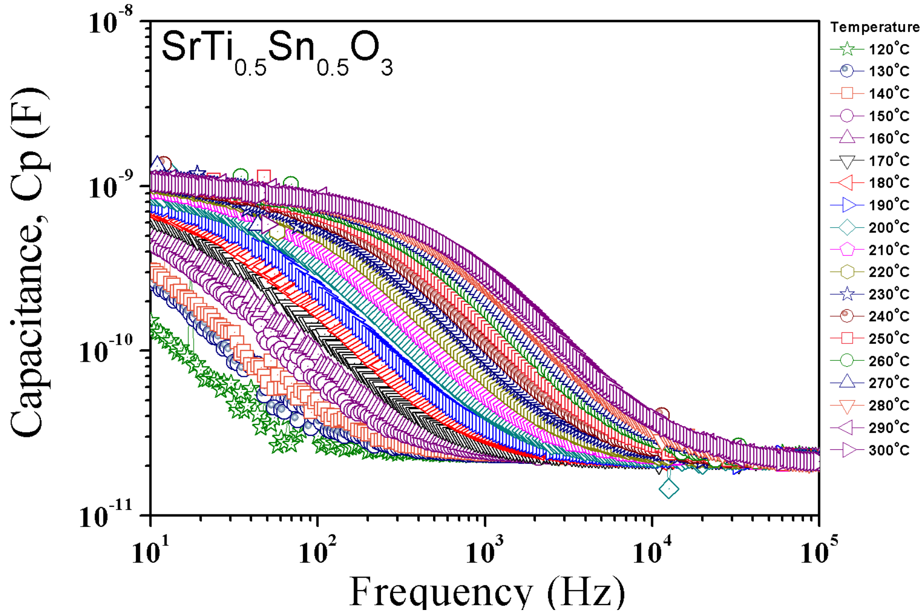

FIGURE 5. Capacitance versus frequency of $SrTi_{0.5}Sn_{0.5}O_3$

The dielectric loss (Fig. 6) decreases by increasing the temperature and frequency whereas spectrum of two set dielectric loss peak for $SrTi_{0.5}Sn_{0.5}O_3$ are observed. First at the initial frequency which tan δ about 10^0 to 10^1 and the second obtained peak at frequency between 10^3 Hz and 10^4 Hz which tan δ about 10^0 to 10^{-2} . This result obtained might be indicating dielectric relaxation from the double ionization of oxygen vacancies or its related defect association like Ti^{4+}/Ti^{3+}- $V_{o^{\cdot}}$ [15] and were usually reported to be associated with oxygen vacancies.

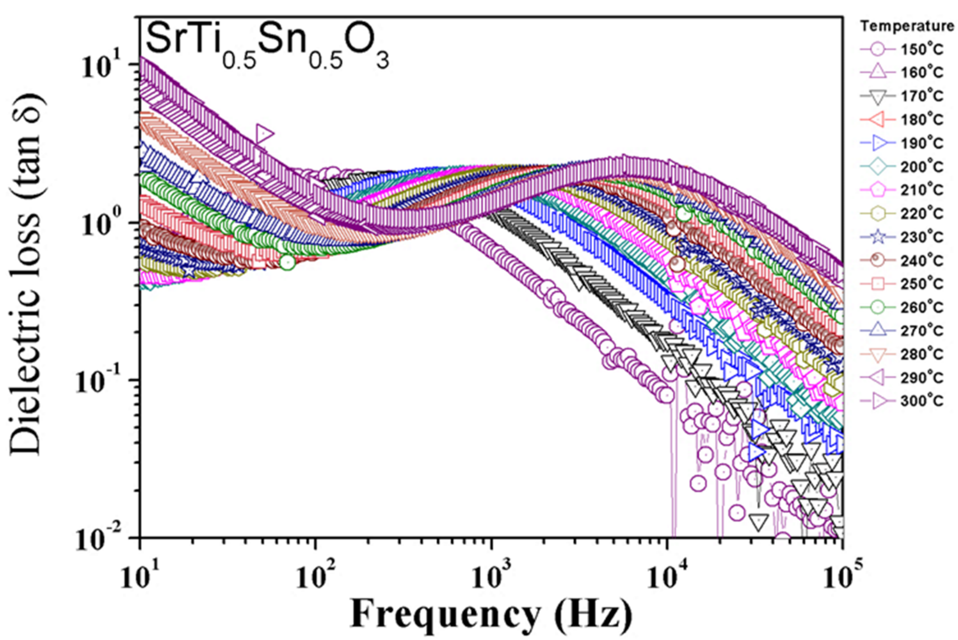

FIGURE 6. Dielectric loss. versus frequency of $SrTi_{0.5}Sn_{0.5}O_3$

CONCLUSION

Sn-doped $SrTiO_3$ sample with 50 mol% Ti/Sn ratios was synthesized by a solid-state reaction. The $SrTi_{0.5}Sn_{0.5}O_3$ shows single phase cubic perovskite structure and no impurity phases were detected. The dielectric constant of strontium titanate is higher at low frequency and higher above 120°C. The highest dielectric constant was about 2000 measured at 10Hz was found for the $SrTi_{0.5}Sn_{0.5}O_3$ sample. $SrTi_{0.5}Sn_{0.5}O_3$ is electrically inhomogeneous with contribution of bulk and grain boundaries.

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