Sol-Gel Synthesis and Impedance Studies of Perovskite $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$ Ceramics

Arun Kumar Yadav[1)], Anita verma[1)], Sunil Kumar[1)], Somaditya Sen[1,2,3,a)]

[1]*Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Khandwa Road, Indore-453552, India*
[2]*Discipline of Physics, Indian Institute of Technology Indore, Khandwa Road, Indore-453552, India*
[3]*Dept. of Electrical Engg., Ming Chi University of Technology, New Taipei, Taiwan*

[a)]Corresponding author: sens@iiti.ac.in

Abstract. Sodium and samarium substituted $PbTiO_3$ ceramics $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$ for x = 0.30 and 0.40 compositions have been synthesized using sol-gel process. The present investigation focus on the temperature-dependent relaxation process and impedance studies of PNST ceramics. Two semicircular arcs were observed in Nyquist plot. Fitting of impedance data using Cole-Cole equation was used to separate the grain and grain boundary contribution to total impedance. The overall conductivity decreases with an increase in substitution. At 410 ºC the conductivity varies from $3.7 \times 10^{-7}\ \Omega^{-1}cm^{-1}$ to $1.9 \times 10^{-7}\ \Omega^{-1}cm^{-1}$ for x = 0.30 to x = 0.40 respectively.

INTRODUCTION

Ferroelectric materials are widely used for commercial applications ranging from high-dielectric-constant capacitors to piezoelectric transducers, positive temperature coefficient devices, and non-volatile ferroelectric random access memories, etc[1, 2]. $PbTiO_3$ is most studied in view of ferroelectric/piezoelectric properties. $PbTiO_3$ has a high Curie point, T_m, (763 K), representing a cubic-tetragonal phase transformation. So it can be used for a large temperature regime. But, dielectric and ferroelectric properties of the pure $PbTiO_3$ phase have been reported in many reports. It is a difficult investigation, due to limitations of preparation of pure phase, sufficiently dense and tough $PbTiO_3$ pellets. Large volume changes at $T_m \sim 763$ K, lead to internal stresses in the pure $PbTiO_3$ pellets[1, 3, 4]. This generates fragile pellets which are difficult to handle during characterization. Also, at the high sintering temperature, Pb starts to evaporate and create the oxygen vacancies in the lattice. Hence, reduce the resistivity of the materials.

$Na_{0.5}Sm_{0.5}$substituted $PbTiO_3$ compounds have been enabled to fabricate the dense ceramics. The detailed temperature-dependent impedance measurement was analyzed for x = 0.30 and 0.40 compositions. Grain and grain boundary contribution was distinguished by the fitting of impedance data using Cole-Cole-equation. Substituted samples showed the increase in resistivity for x = 0.40 compare to x = 0.30 composition.

SYNTHESIS OF MATERIALS

A polycrystalline $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$ (x = 0.30 and 0.40 compositions)(named as: PNST) ceramics were fabricated *via* modified sol-gel process. Precursors used to synthesize these materials are lead nitrate ($Pb(NO_3)_2$), sodium nitrate, samarium oxide and titanium (IV) bis(ammonium lactato) dihydroxide solution. Precursors were chosen on the basis of solubility in deionized water or diluted nitric acid. Samarium oxide was dissolved in dilute nitric acid. Solutions of individual cations were prepared in separate beakers. The samarium and titanium solutions were mixed followed by sodium and lead. Stirring for two hours of the resultant solution ensured perfect mixing. A solution of citric acid and ethylene glycol of 1:1 molar ratio was prepared to serve as a gel former. This solution was then added to the solution containing the cations. Rigorous stirring for an hour followed along with heating at ~ 85 ºC. The gels were burnt to form black powders. These black powders were ground and heated at 500 ºC for 12 h to de-carbonate and de-nitrate. Thereafter the powders were re-grinded and heated at 700 ºC. The powders were re-grinded, mixed with 5 wt %polyvinyl alcohol (PVA) binder solution and uni-axially pressed into pellets (diameter ~13 mm; thickness ~1.5 mm). The pellets were sintered at 600 ºC for 6 h to burn out the PVA binder. The relative density of the pellets was optimized by further appropriate heating at 1050 ºC for 6 h. Relative density ~ 93 % and ~ 94 % have been obtained for x = 0.30 and x = 0.40 compositions respectively.

Electrodes were prepared using high-temperature silver paste painted on both sides of the sintered pellet which were cured at 550 °C for 15 minutes. Before we started the measurement, surface moisture was removed by heating the samples at 200 °C for 10 minutes. A Newtons 4th Ltd. PSM 1735 LCR meter was used to study the dielectric properties.

RESULTS AND DISCUSSION

The grain and grain boundary quantitative contribution of polycrystalline PNST ceramics are studied using the ac impedance spectroscopy. Generally, a polycrystalline material provides grain and grain boundary properties with different time constants leading to two successive semicircles. Z" (capacitive) versus Z' (real impedances) are the two components of the complex impedance Z. In general Z" versus Z' plots reveal two clear semicircles. Higher frequency semicircle can be attributed to the grains while lower frequency semicircle to the grain boundary[5]. The impedance of a such system can be analyzed by the Cole-Cole equations [6].

$$Z^*(\omega)=\frac{R_1}{1+\left(j\omega\tau_g\right)^{1-\alpha_g}}+\frac{R_2}{1+\left(j\omega\tau_{gb}\right)^{1-\alpha_{gb}}} \qquad (1)$$

The real (Z') and imaginary (Z") parts of impedance can be written in the following manner also subscript g and gb representing the grain and grain boundary notation respectively:

$$Z'(\omega)=\frac{R_1\left[1+\left(\omega\tau_g\right)^{1-\alpha_g}\sin\left(\frac{\alpha_g\pi}{2}\right)\right]}{1+2\left(\omega\tau_g\right)^{1-\alpha_g}\sin\left(\frac{\alpha_g\pi}{2}\right)+\left(\omega\tau_g\right)^{2-2\alpha_g}}+\frac{R_2\left[1+\left(\omega\tau_{gb}\right)^{1-\alpha_{gb}}\sin\left(\frac{\alpha_{gb}\pi}{2}\right)\right]}{1+2\left(\omega\tau_{gb}\right)^{1-\alpha_{gb}}\sin\left(\frac{\alpha_{gb}\pi}{2}\right)+\left(\omega\tau_{gb}\right)^{2-2\alpha_{gb}}} \qquad (2)$$

$$Z''(\omega)=\frac{R_1\left(\omega\tau_g\right)^{1-\alpha_g}\cos(\frac{\alpha_g\pi}{2})}{1+2\left(\omega\tau_g\right)^{1-\alpha_g}\sin\left(\frac{\alpha_g\pi}{2}\right)+\left(\omega\tau_g\right)^{2-2\alpha_g}}+\frac{R_2\left(\omega\tau_{gb}\right)^{1-\alpha_{gb}}\cos(\frac{\alpha_{gb}\pi}{2})}{1+2\left(\omega\tau_{gb}\right)^{1-\alpha_{gb}}\sin\left(\frac{\alpha_{gb}\pi}{2}\right)+\left(\omega\tau_{gb}\right)^{2-2\alpha_{gb}}} \qquad (3)$$

Where, τ_g and τ_{gb} are the characteristic times for the grain and grain boundary conduction contribution process. Also Cole-Cole parameters $\alpha_g=\frac{2\theta_g}{\pi}$ and $\alpha_{gb}=\frac{2\theta_{gb}}{\pi}$ are the measure of the distribution of characteristics times associated with the grain and grain boundary, where θ_g and θ_{gb} are the angles of depression of the semicircle centers.

The Z'-Z" plots for PNST ceramics at lower temperatures due to very high resistance do not show a double semicircular nature. A linear plot was obtained instead. Hence both the resistance and dielectric dispersion effect were not obtained simultaneously. At a higher temperature, we could obtain a better double semicircular nature (Fig. 1). A comparison of these two compositions shows a higher resistance for x = 0.40 sample. The resistance is found to decrease for both the compositions with increasing temperature. This is the characteristic of the polycrystalline ceramic material to decrease the resistance with increasing temperature.

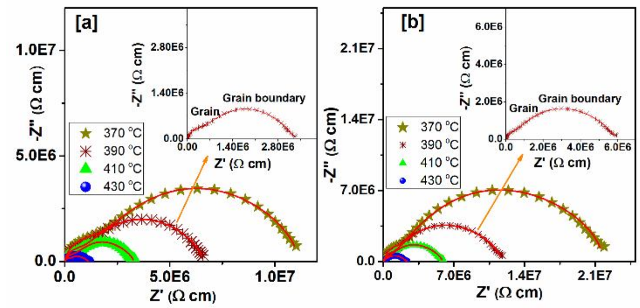

Figure 1. Cole-Cole plots at different temperatures for PNST ceramics for (a) $x = 0.30$, and (b) $x = 0.40$. Grain and grain boundary contribution of each sample (inset); Symbols: experimental data, whereas, red line: Cole-Cole fitting.

The real part of impedance, Z', is higher at lower frequencies than at higher frequencies (Fig. 2). The value of Z' decreases with rising temperature for lower frequencies. For $x = 0.40$, Z' is higher than $x = 0.30$ composition. At higher frequencies, Z' becomes invariant for all the temperatures and frequencies. This can be explained as the release of space charge with the increase in temperature and is responsible for the decrease of Z' values. Conductivity increases with the increase of temperature for both compositions[7-9].

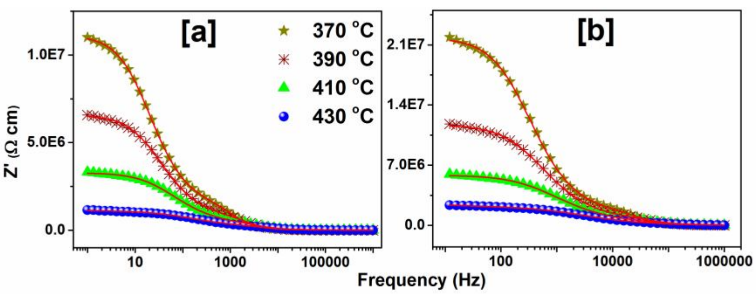

Figure 2. Variation of real part of impedance, Z', with frequency at different temperatures for PNST ceramics for (a) $x = 0.30$ and (b) $x = 0.40$ compositions. Symbols: experimental data, whereas, red line: Cole-Cole fitting.

Variation of the imaginary part of impedance (Z'') with frequency at different temperatures are shown in Fig. 3. It is perceived that fitted data and experimental data with Cole-Cole equation are in good agreement with the relaxation process in these samples for the entire frequency range. Two peaks are observed for each temperature for both compositions corresponding to the grain and grain boundary related contribution. With increasing temperature, the peaks shift to higher frequencies, and the intensity is suppressed; a clear indication of decreasing the resistance in both samples. A comparison of grain and grain boundary resistance after fitting with the Cole-Cole equation at different temperatures are provided in Table 1. At a particular temperature, grain resistance is less and grain boundary resistance is more for $x = 0.40$ compare to $x = 0.30$ composition.

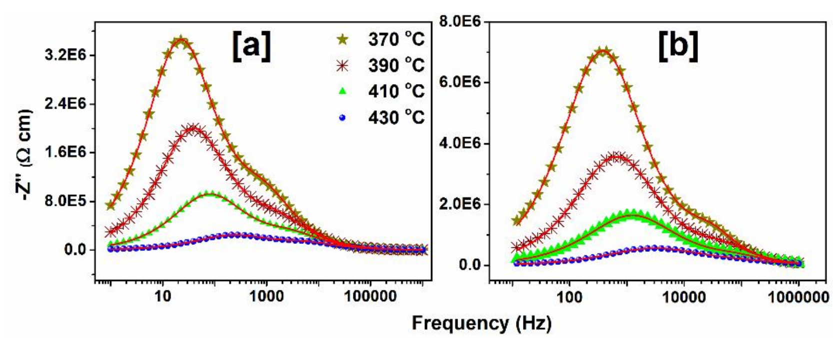

Figure 3. Variation of imaginary part of impedance, Z'', with frequency at different temperatures for PNST ceramics for (a) $x = 0.30$ and (b) $x = 0.40$ compositions. Symbols: experimental data, whereas, red line: Cole-Cole fitting.

Table1. Quantitative values of grain and grain boundary resistance after fitting with Cole-Cole equation of $Pb_{(1-x)}(Na_{0.5}Sm_{0.5})_xTiO_3$ ceramics for x = 0.30 and x = 0.40 compositions.

	Grain resistance (Ω cm)				Grain boundary resistance (Ω cm)			
Compositions	370 ºC	390 ºC	410 ºC	430 ºC	370 ºC	390 ºC	410 ºC	430 ºC
x = 0.3	1.588E6	878950	464201	211597	8.573E6	5.022E6	2.2319E6	657779
x = 0.4	1.336E6	751191	373231	192226	1.862E7	9.7629E6	4.691E6	1.685E6

CONCLUSIONS

We have successfully synthesized PNST ceramics using the sol-gel method. Temperature and frequency dependent electrical properties of these ceramics were studied using the impedance spectroscopy. Temperature-dependent relaxation is observed in these ceramics. Double semicircles were observed in the Cole-Cole plots corresponding to grain and grain boundary contribution. Grain resistance is found to decrease and grain boundary increase for x = 0.40 compare to x = 0.30 composition. Overall resistance is increased for x = 0.40 compare to x = 0.30 substitution.

ACKNOWLEDGMENTS

Author, Arun Kumar Yadav is thankful to University Grants Commission for fellowship (NFO-2015-17-OBC-UTT-28455). The authors are thankful to Indian Institute of Technology, Indore for funding the research. Special acknowledgement goes to Sophisticated Instruments Centre (SIC), IIT Indore for the elementary characterizations.

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