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COMPLEX IMPEDANCE STUDIES ON LAYER STRUCTURED LANTHANUM SUBSTITUTED SBT CERAMICS

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ABSTRACT

The impedance measurements have been performed in the temperature range 30 °C to 600 °C and the frequency range 500 Hz to 1 MHz on lanthanum doped four-layered $SrBi_{4-x}La_xTi_4O_{15}$ (SBLT) with x = 0.05, 0.1, 0.25, 0.5, 0.75. These samples show strong frequency and temperature dependent dielectric relaxations. Peaks appear in Z" versus frequency plots and they shift towards higher frequency side with increasing temperature. Similar behavior was observed in M" Vs frequency plots. As the temperature increased, the peaks tend to sharpen and all the curves appear to merge at high frequencies. The relaxation times were calculated from the peak value of Z" Vs frequency and evaluated activation energies. The imaginary components of impedance Z" and the electrical modulus M" have been computed, both as a function of frequency and temperature.

Keywords: SBT, Impedance spectroscopy, Dielectric, Layer structured.

1. INTRODUCTION:

BLSF materials generically described as $M_{n-1}B_nO_{3n+1}$, where both M and B are ions with suitable chemical valence and ionic radii, as for example $M=Bi^{3+}$, Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, K^+ or rare-earth elements, $B=Ti^{4+}$, Nb^{5+}, Ta^{5+}, Fe^{3+}, or Ga^{3+}. The structures comprise perovskite-like $\left(M_{n\text{-}1}\,B_nO_{3n+1}\right)^{2-}$ slabs regularly interleaved with $\left(Bi_2O_2\right)^{2+}$ layers, where *n*=1,2,3,4... There has been considerable interest in the potential of bismuth titanate ($Bi_4Ti_3O_{12}$) as high temperature piezoelectric sensor, which has small dielectric constant and low dielectric loss tangent. The addition of $SrTiO_3$ to the $Bi_4Ti_3O_{12}$ results into a material, which can be electrically poled easily and exhibits very stable dielectric and piezoelectric properties [1]. It also results in the formation of compounds with a large number of Perovskite units, with increasing Sr concentration, such as $SrBi_4Ti_4O_{15}$, $Sr_2Bi_4Ti_5O_{18}$ and $SrBi_8Ti_7O_{27}$ within two consecutive bismuth oxide layers. The $SrBi_4Ti_4O_{15}$ (SBT) belong to this family with n=4. In the present work bismuth in $SrBi_4Ti_4O_{15}$ is partially replaced with La^{3+} to synthesize $SrBi_{4\text{-}X}La_X\,Ti_4O_{15}$ and the results of Impedance spectroscopy studies of the prepared materials.

2. EXPERIMENTAL:

Polycrystalline samples of SBLT with x = 0.05, 0.1, 0.25, 0.5, 0.75 were prepared through a chemical route. The stoichiometric amounts of $SrCO_3$ and La_2O_3 were taken and converted to their respective nitrates by adding nitric acid solution. Bi $(NO_3)_3{\cdot}5H_2O$ was added along with TiO_2. The entire mixture was slowly heated on a hot plate and citric acid was added. The pH was adjusted to 6-7 by adding dilute ammonium hydroxide solution. Ethylene glycol was added and heated over the temperature 160-180 °C to get the gel. The gel was heated to obtain the precursor. This precursor was heated at 800 ^oC for 2 hours. The resultant powder was crushed and pressed in the form of pellets of 10 mm of dia using polyvinyl alcohol as the binder. The pellets were finally sintered in the temperature 1200 ^oC for 2 hours. The resultant samples were characterized by powder XRD (PW3040/60 X'pert PRO). The samples were electroded on both sides using silver paste and dried at 180^oC. The impedance properties were measured as a function of temperature from room temperature upto 600^oC at different frequencies (500 Hz to 1 MHz) using Auto Lab PG STAT 30. The data acquisition is automated with a PC interfaced to this instrument.

3. RESULTS AND DISCUSSION:

Figure 1 shows variation of imaginary part of impedance (Z'') with frequency at different temperatures. The Z'' value increases initially reaches maxima ('Z^P' peak value) and then decreases with frequency. This, Z^P value decreases with increasing temperature and the peak position shift to high frequency side. As the temperature increases, the peaks tend to broaden. The broadness of the peak indicates multiple relaxations in the material. These multiple relaxations may be due to fluctuation in the structure because of random occupation of lanthanum and bismuth in equivalent sites. All the curves appear to merge at high frequencies. This may be due to the presence of space charges in the sample. The Z^P value decreases with increasing temperature denoting the increase in capacitance and decrease in resistance of the material indicating the increase in conductivity.

Figure 2 shows the complex impedance plots. Z'' Vs Z' plots are more or less inclined with respect to Z''- axis line in the temperature regions 30 ^oC to 475 ^oC. The Cole-Cole plots are semicircles in the temperature regions 500 ^oC to 600 ^oC. The center of the semicircles below the real axis indicates the deviation from Debye behaviour. In the present system of samples, complex impedance spectra shows single semi-circle and the radius of semi-circle decreases with increase of temperature. At the maximum of the semicircles, $\omega\tau = 1$. The relaxation time is calculated from frequency variation of Z'' and is plotted as a function of inverse of temperature (fig. 3) from these curves and these relaxation times decreases with increase of temperature.

It is impossible for any system to have a single relaxation time [2]**.** Normally a material contains different types of dipoles, each of which has a relaxation time different from others. Hence the Cole-Cole plots in practice, are not exactly semicircular, but are distorted. (to varying degrees.). The centres of these semicircles are depressed below the real impedance axis by an angle and intersect the Z'- axis [3]**.** The mean relaxation time is the inverse of peak frequency. In polycrystalline materials in addition to the arc for dielectric relaxation with in the grains, (bulk relaxation), another arc due to the partial or complete blocking of charge carriers at the grain boundary may also be formed. Generally the electrode processes relax at low frequencies, grain boundaries relax at intermediate frequencies and the relaxation due to the grain of the sample occurs at higher frequencies.

In general one or more of four representations are used to represent data in the complex plane. These four complex formalisms, the impedance $Z*$, the electric modulus $M*$, the admittance $Y*$, and the permittivity $\varepsilon*$ and these are interrelated [4]

$$Z^* = Z' - jZ''$$
$$Y^* = Y' + jY'' = j\omega C_o \varepsilon^*$$
$$M^* = M' + jM'' = j\omega C_o Z^*$$
$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \left(M^*\right)^{-1}$$

The above four expressions offer wide scope for graphical analysis. The popular forms of data presentation are complex impedance plots (Z' vs Z''), loss spectra (ε' or M' or Z'' vs frequency) and the plots of $\varepsilon', \varepsilon'', \sigma', \sigma''$ vs frequency. Polycrystalline materials posses both large grain boundary resistances and small crystal resistances. The grain boundary resistance dominates the AC response in the complex impedance plane and completely mask the effect of bulk resistance. In the complex electric modulus method, importance is given to those elements that have smallest capacitance. In this case, the response of the crystal dominates the behaviour whereas the grain boundary effects may be masked.

$$\begin{aligned} Z^* &= \left(\frac{1}{\mathrm{R}} + j\omega C\right)^{-1} \\ &= \frac{R}{1 + j\omega RC} \\ &= \frac{R}{\left(1 + (\omega RC)^2\right)} - \frac{R^2 j\omega C}{\left(1 + (\omega RC)^2\right)} \\ &= \frac{R}{\left(1 + (\omega\tau)^2\right)} - \frac{R^2 j\omega C}{\left(1 + (\omega\tau)^2\right)} \\ &= Z' - jZ'' \end{aligned}$$

Above equation can be rearranged to obtain [5]

$$(Z' - R/2)^2 + (Z'')^2 = R^2 / 4$$

This is the equation of a circle with a radius $R/2$ and center ($R/2$, 0). The co-ordinates at the top of the semicircle are ($R/2, R/2$). The values of Z' and Z'' plotted on a linear scale as complex plane diagram take the form of semicircles known as Cole-Cole plots [6] as shown in fig. 2. Similar plots can be obtained for M'' Vs M' data (fig. 5b).

The variation of AC conductivity $\left(\sigma_{\mathrm{a.c.}}\right)$ as a function of frequency at different temperatures on log-log plot shows (fig. 4) an increase of $\left(\sigma_{\mathrm{a.c.}}\right)$ with increase of frequency. This dependence is generally expressed as $\sigma_{\mathrm{a.c.}} = \left(\sigma_{\mathrm{o}} + \mathrm{A}\omega^{\mathrm{n}}\right)$ where A is constant, $\omega = 2\pi f$, f is angular frequency and '*n*' is exponent [7]**.** The exponent '*n*' is varying with temperature. The AC conductivity plots of present measurements show two distinct slopes indicating that '*n*' can be written as $n = n_1 + n_2$. This means two different processes of conduction are present in the samples. These conduction processes are frequency dependent. The values of n_1 & n_2 decrease with increase of temperature. (not shown). AC conductivity depends significantly on the frequencies at lower temperature region as usually observed in this type of materials [8]**.** With increase in temperature, the dielectric relaxation takes place and the dependence of conductivity on frequency is less prominent. It is found that the plots merge at higher frequency range. Increasing of La^{3+} content in $SrBi_{4-x}La_xTi_4O_{15}$ gives increased AC conductivity.

The impedance data can be analyzed much better by replotting them in the modulus formalism. This complex modulus plots give complementary information to the information given by the impedance plots. The modulus data are calculated in the form of imaginary part of modulus, M'' and real part, M' by using the relation $M' = \omega C_o Z''$ and $M'' = \omega C_o Z'$ (ω, is angular frequency $2\pi f$, C_o the vaccum capacitance of the measuring cell and electrodes with an air gap in place of the sample). Typically modulus plots of these samples are shown in figure 5a, 5b in the temperature range 525 ^{o}C to 600 ^{o}C. It is observed that the increasing of temperature area of the semicircle is increasing.

The plots of M'' against the logarithm of the frequency, gives rise to a Lorenztian peak in the ideal case of a single time constant (in real systems the peaks are broader and asymmetrical). Figure 5a shows variation of imaginary part of modulus (M'') with frequency at different temperatures. The M'' value increases initially reaches maxima ('M^P' peak value) and then decreases with frequency. M^P value increases with increasing temperature and the peak position shift to high frequency side. As the temperature increases, the peaks tend to sharpen. All the curves appear to merge at high frequencies.

4. CONCLUSIONS:

Lanthanum doped four-layered SBT with x = 0.05, 0.1, 0.25, 0.5, 0.75 were prepared through chemical route. Impedance spectroscopic studies were done. Modulus spectroscopy parameters such as M'' and M' were calculated from the impedance data. Relaxation times and activation energy for relaxation were calculated.

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TABLE

Table 1.

Composition (x)	A.E. for τ_z (in eV)	A.E. for τ_M (in eV)
0.05	1.51	1.71
0.1	1.75	1.82
0.25	1.21	1.07
0.5	0.85	0.70
0.75	0.74	0.61

A. E. – Activation energy for relaxation.

FIGURES

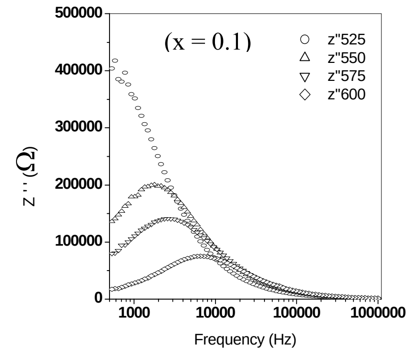

Fig. 1a Z ' ' Vs Frequency

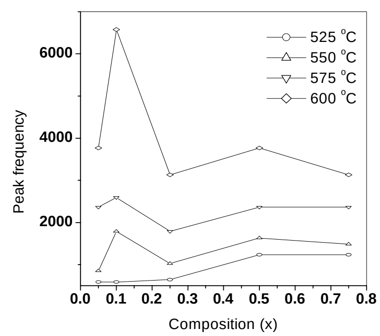

Fig.1b Peak frequency Vs Composition(x)

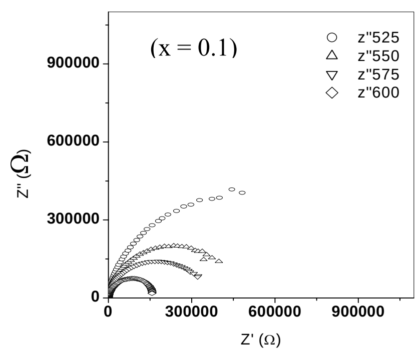

Fig. 2 Z ' ' Vs Z '

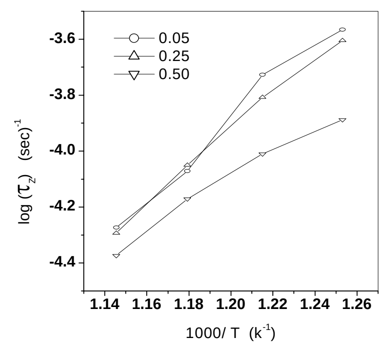

Fig.3a τ_Z Vs 10^3/T

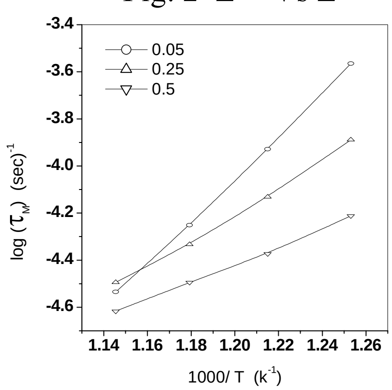

Fig.3b τ_M Vs 10^3/T

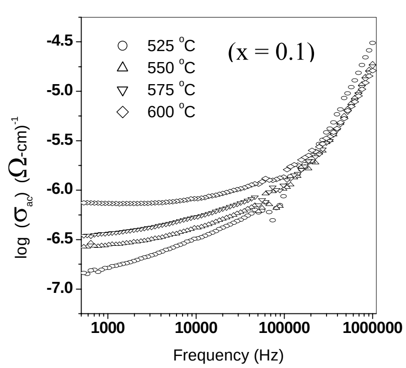

Fig.4 log (σ_{ac}) Vs Frequency

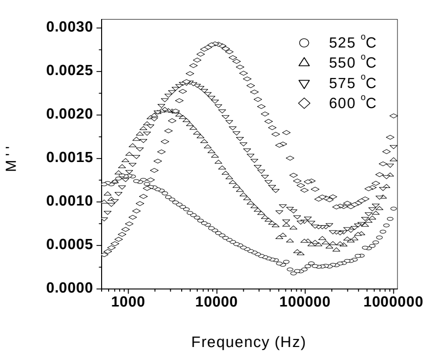

Fig. 5a M ' ' Vs Frequency (x = 0.1)

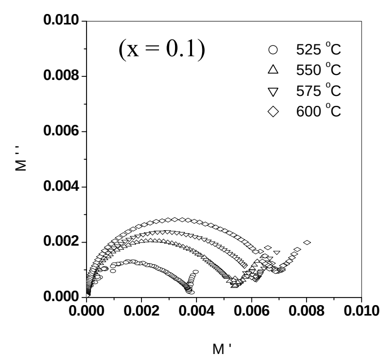

Fig. 5b M ' ' Vs M '