Impedance spectroscopic studies in SrBi$_4$Ti$_4$O$_{15}$

N Venkat Ramulu, M Aparna, G Prasad, G S Kumar & T Bhima Sankaram

Materials Research Laboratory, Department of Physics, Osmania University, Hyderabad 500 007

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The impedance measurements have been performed in the temperature range of 30 to 600 °C and the frequency range 1 kHz to 10 MHz on four-layered SrBi$_4$Ti$_4$O$_{15}$. The imaginary components of impedance $Z''$, the electrical modulus $M'$ and ac conductivity have been computed, both as a function of frequency and temperature. The peaks appear in $Z''$ versus frequency plots and they shift towards lower frequencies at the temperature up to 500 °C and above 525 °C they shift towards higher frequencies. Similar behaviour is observed in $M'$ versus frequency plots. $Z''$ values decrease with increase of temperature, while $M'$ values decrease up to 500 °C and above 525 °C these values are found to increase with temperature. Complex impedance diagrams are nearly semicircles at higher temperatures. Results are interpreted in terms of possible conductivity mechanisms present in the sample.

1 Introduction

Bismuth-layer structured ferroelectrics are an important class of lead free ferroelectric compounds with general formula (Bi$_2$O$_3$)$_x$ ($A_{n-1}B_nO_{3n+1}$)$_y$, e.g. Sr$_n$Ti$_{3n}$, Ba$_n$Ti$_{3n}$, Sr$_{2n+1}$Ti$_{4n}$, etc. As in other types of ferroelectrics these compounds also have the presence of ions of small size and large charge (e.g. Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$, etc.) in oxygen octahedra, which are linked through corners forming continuous chains of oxygen-metal-oxygen. Such a structural arrangement is favorable for the occurrence of ferroelectricity in oxides.

Ito et al. synthesized several compounds in this family and examined their crystal structure. The structure comprises a stacking of $m$-perovskite like units of normal composition ABO$_3$ between Bi$_2$O$_3$ layers along the pseudo-tetragonal c-axis. It is noteworthy that the continuous extension of the O-M-O chains along the c-axis is interrupted not only by the presence of Bi$_2$O$_3$ layers but also by the translation of the perovskite units in the plane perpendicular to the c-axis. Bismuth layer structure ferroelectrics (BLSF) in general have relatively high Curie temperatures, high coercivity, low dielectric dissipation factor, high anisotropy and dielectric strength. These compounds find applications in ferroelectric random access memory (FRAM) with high fatigue endurance and in high temperature piezoelectric sensors. Fatigue in ferroelectric devices has been studied for several years and several mechanisms have been proposed to explain this degradation phenomenon.

There has been considerable interest in the potential of bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) as high temperature piezoelectric sensor, which has small dielectric constant and low dielectric loss tangent. The addition of SrTiO$_3$ to the Bi$_4$Ti$_3$O$_{12}$ results into a material, which can be electrically poled easily and exhibits very stable dielectric and piezoelectric properties. It also results in the formation of compounds with a large number of perovskite units, with increasing Sr concentration, such as SrBi$_3$Ti$_5$O$_{25}$, Sr$_2$Bi$_4$Ti$_7$O$_{24}$, and Sr$_3$Bi$_4$Ti$_{17}$O$_{33}$, within two consecutive bismuth oxide layers. In this paper a study of impedance spectroscopy of the conventionally sintered polycrystalline samples of SrBi$_3$Ti$_5$O$_{25}$ has been presented. The molecular formula of the compound studied is Bi$_6$O$_{12}$ 4(Bi$_{3/4}$ Sr$_{1/4}$ TiO$_3$). Here is un-occupancy in A position of the perovskite (ABO$_3$) structure of the layer compound.

2 Experimental Details

The Polycrystalline sample SrBi$_3$Ti$_5$O$_{25}$ was prepared by employing solid state reactive sintering. The initial compounds SrCO$_3$, Bi$_2$O$_3$, and TiO$_2$ of AR-grade with 99.99% purity were mixed in appropriate ratios. The mixture was thoroughly grounded and the particle size of the starting materials was of the order of one micron. The mixture was stacked in a crucible and sintered isothermally in air at 850 °C for two and half hours.
and then furnace cooled. The material so formed was crushed and powdered by repeated grinding in the ethanol medium. Pellets were made by pressing the powder into cylinders (dia 1.2 cm and height 1-2 mm) at a pressure of 10 Mpa. Sample was finally sintered at 1100 °C for 2 hrs. The entire sintering protocol was carried out in a temperature-controlled furnace.

2.1 X-ray diffraction

X-ray diffractogram of the powder samples were taken using Cu-Kα radiation at a scanning speed of one degree per min (Fig. 1). Formation of a single-phase material was confirmed by unambiguously indexing of all the recorded peaks on the basis of a distorted tetragonal cell. The lattice constants a, b and c were evaluated. Using this data X-ray densities were computed and compared with those experimentally determined. The experimental density of the sample was found to be above 95% of the X-ray density.

2.2 Poling procedure

Sample was poled electrically prior to the dielectric measurements. The poling was done at 150 °C under a dc field of 20 KV/cm and cooled to room temperature rapidly in the presence of the field. Poling above 150 °C was not possible due to increased conductivity of the sample.

2.3 Electrical measurements

The dielectric and impedance measurements were made in the frequency range of 1 kHz-10 MHz and in the temperature range of 30 to 600 °C. The
large faces of the pellets were initially coated with silver paint and dried at 110 °C. Data were collected in steps by using a HP-4192A impedance analyzer interfaced to a computer. The acquisition of data at still higher temperatures was restricted by the enhanced conductivity of the samples. The dielectric constant was determined by measuring the capacitance of the electrically poled sample, at fixed frequencies of 10, 50 and 100 kHz, with increasing temperature up to 600 °C.

3 Results and Discussion

Fig. 2 shows the temperature dependence of the dielectric constant (Fig. 2(a)) and loss tangent (Fig. 2(b)) studied at three different frequencies. The dielectric constant versus frequency plots show a peak at 530 °C, which corresponds to the Curie temperature and the transition temperature is in close agreement with reported results. The value of dielectric constant at the peak decreases with the increasing frequency. The magnitude of decrease is large at lower frequencies and small at higher frequencies and appears to tend to a saturation value. Dielectric loss tangent (Fig. 2(b)) shows a peak at lower temperatures and the peak temperature corresponds to the shoulder of the peak observed in dielectric constant versus temperature graph. Dielectric loss also decreases with the increase in frequency and the magnitude of decrease is larger at lower frequencies. Dielectric constant

![Graphs](image-url)
and loss tangent show little variation with temperature up to about 400 °C.

![Graph](image)

**Fig. 4** — Peak frequencies as a function of temperature

The impedance data is analyzed in terms of four parameters, the impedance $Z^* = Z - jZ''$; the electric modulus $M^* = j\omega C Z^*$ where $\omega$ is the angular frequency, $C_0$ is the free space capacitance of the sample cell with air gap in place of sample. Variations of the typical impedance parameters ($Z''$ and $M''$) with frequency (in the temperature ranges indicated) are given in Figs 3(a), (b), (c) and (d). It is convenient to divide the measurements into two graphs, one corresponding to the temperature below 500 °C, as shown in Figs 3(a) and (b), and the other corresponding to temperature close to the Curie point (>525 °C) and above, as shown in Figs 3(c) and (d). From the position of peaks the relaxation times are calculated using the relation $\tau = 1$. The modulus plots lay emphasis on elements of the ceramics with smallest capacitances, while impedance plots highlight the elements with largest resistance. Hence the modulus plots show an increase in values of $M'$ and $M''$ with the increase in frequency which is consistent with decreasing $Z'$ and $Z''$ values with increasing frequency.

The experimental data was obtained at different set temperatures of the sample. The $Z''$ and $M''$ plots show peaks in the frequency range and temperature range studied. The peak position in the frequency plot (Fig. 4) shifts to higher frequencies as the temperature of the sample is raised. The frequency variation curves become broader at higher temperatures. From the peak maxima, the values of $\tau_e$ and $\tau_m$ have been calculated and are found to be dependent on temperature.

![Graph](image)

**Fig. 5** — Variation of relaxation time as a function of inverse of temperature

Inverse of this maxima frequency $\tau_e$ is calculated and plotted as a function of inverse of temperature (Fig. 5(a)) and this parameter appears to follow the Arrhenius relation $\tau_e = \tau_{e0} e^{E/kT}$ with $E = 0.62 \pm 0.05$ eV and $\tau_{e0} = 7.96 \times 10^9$ s. A similar plot (Fig. 5(b)) from impedance versus frequency graphs for $\tau_m$ (inverse of the peak frequencies of $M''$ versus frequency graphs) have activation energy $E = 0.17 \pm 0.05$ eV and $\tau_m = 1.46 \times 10^9$ s. It should be remembered that the ac conductivity process is
dependent on the capacitance of the sample. The relaxation times obtained from the peak frequency explicit plots of $Z'$, $M''$ and $\tan\delta$ are respectively given as $\tau_c$, $\tau_m$, $\tau_r$, and $\tau_{\text{rad}} = \tau / \sqrt{r}$, where $r$ is the relaxation ratio and is given by $(\varepsilon_r/\varepsilon_\infty)$. The relaxation ratio $r$ plays a vital role in determining the value of the relaxation time and therefore determines at what frequency the imaginary part of a particular dielectric function will have a peak. The present results indicate that $\tau_c > \tau_m$ and the values of relaxation ratio ($r$) is given by $\tau / \tau_c = 1 / r$ and is found to be within 2.5 to 14 for SBT samples in the temperature range of present measurements. It is seen that $Z'$ and $M''$ peaks shift to lower frequencies as the temperature is increased in the temperature range below 500 °C. In the temperature range 525 °C and above, it is observed that both $Z'$ peaks as well as $M''$ peaks shift to higher frequencies. $Z'$ and $M''$ peaks are broad indicating multiple relaxations and deviation from Debye behaviour. Both the peaks represent the same physical relaxation phenomenon.

The data when plotted in complex plane $Z''$ versus $Z'$ (Figs 6(a) and (b)) and $M''$ versus $M'$ [(Figs 6(c) and (d)] give an idea about the resistive, capacitive and relaxation behaviour of the charge
entities in the sample. The resistance of the sample (ac and dc) is given by the intercept of the impedance plots ($Z'$ versus $Z$) and capacitance of the sample is represented by the intercept of the plots on the $M'$-axis at high frequency side in $M'$ versus $M''$ plots. The plots are more or less semicircles. The values of $\varepsilon'/\varepsilon_0$ are calculated from the plots of Fig. 6(b) and the values are plotted as a function of temperature (Fig. 7). This plot shows minima around 510 °C, which is close to the transition temperature. The data appear to be useful for finding the transition temperatures as well as the conductivity behaviour. Thus the ac impedance data helps us to find the dielectric behaviour of the sample before and after the transition temperature.

![Fig. 7 — Plot of capacitance ($\varepsilon'/\varepsilon_0$) versus $10^3/T$](image)

The ac conductivity data is extremely useful when the conduction is related to localized hopping of charge species. The real part of conductivity as a function of frequency at different temperatures is plotted in Fig. 8. The conductivity plots show that the conduction in these samples is thermally activated. The ac conductivity is sum of two terms, $\sigma = \sigma_d + \sigma' (\omega)$ and $\sigma' (\omega) = A \omega^n$, where $\sigma_d$ is the conductivity under direct current, $A$ is a constant which is a function of temperature and $\omega$ is the angular frequency. From these plots on the low frequency side, $n$ comes out to be 0.8 to 0.9. As already stated the conduction in the present sample is a thermally activated process. The variable $A$ is a function of temperature and it depends on number of sites available for the charge carriers for hopping.

![Fig. 8 — Plot of log ($\sigma_d$) versus frequency at different temperatures](image)

As we have evidence for localized relaxations, the conduction can be due to barrier hopping. In such a case the charge displacement within the sample is by discrete hops of length $R$ between randomly distributed localized sites. Analysis of
polarization moments is associated with the formula:

$$\alpha'(\omega) = \frac{N^2}{2} \frac{\alpha(R) p(R)}{1 + \omega^2 \tau^2} dR$$

where \(N\) is the number of sites per unit volume, \(\alpha(R)\) is the polarizability and \(p(R)\) is the probability of the another site being located at a distance between \(R\) and \(R + dR\). The relaxation time \(\tau\) is the time associated with a hop distance of \(R\).

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$$R = \frac{C}{E_s W_m} \left[ \frac{1 - 2kT\log \left( \frac{\tau}{\tau_0} \right)}{W_m} \right]^{-1}$$

where \(C\) is a constant and \(E_s\) is related to the distance between the oxygen sites in the octahedra in perovskite structure. \(W_m\) is the energy required for transporting a charge from infinity to the site under consideration and is the activation energy obtained from dc Arrhenius plot. The conduction species (charge carriers) have to cross a potential barrier \(W\) separating two sites. At lower temperatures, the bulk samples can have two mechanisms of conduction. One due to long-range ac conduction and the other due to localized transport of the charges, which are bound. Bindings of the charges arise due to dipolar interaction (Coulomb interaction) between the charge carrier and the ion in the lattice.

The polarization and conductivity variation of a sample is associated with the displacement of the charge carriers, which move within the sample by discrete jumps between two localized sites separated by a distance.

The charge mobility is caused by thermally activated process and involves crossing of the potential barrier \(W\) separating two sides. This mechanism is associated with a relaxation time given in the form:

$$\tau = \tau_0 \exp \left( \frac{E}{kT} \right)$$

The relaxation times are calculated from the peaks of \(Z'\) or \(M'\) plots and log \(\tau\) thus obtained is plotted as a function of \(10^3/T\) as shown in Fig. 5. The activation energy comes out as 0.62 eV. The relaxation time is associated with the CBH (correlated barrier hopping) model. The height of the barrier \(W_m\) is related to the distance \(R\) as:

Fig. 9 — Plot of log (\(Q_{dc}\)) versus \(10^3/T\)

The dc conductivity plot (Fig. 9) indicates that there are two slopes above 250 °C. At lower temperatures the data tends to deviate from the straight line. Grain boundary effects and defect ion complexes, or charge carrier-ion complexes in the ceramics influence the conduction at lower temperature. This is evident from \(M'\) frequency explicit curves. At lower frequencies there is a peak and the peak represents capacitance inverse. The magnitude does not change much with temperature. Therefore it is natural to infer that this capacitance indicated at lower frequencies should be associated with grain boundaries, other than the bulk of the grains. The low values of \(M'\) at these frequencies also indicate large capacitance values. The grain boundary effects and dipole complexes control the activation process at lower temperatures. At higher temperatures the dipoles may disassociate and contribute to long-range conductivity. The peak values in \(M'\) curve at higher frequencies appear to change with temperature and hence the capacitance would increase with temperature appreciably. The relaxation time also changes with temperature. As the peaks appear to have shifted beyond the range of frequency of the ac field applied it is not possible to predict variation of \(\tau_0\) associated with these peaks.
In conclusion, the study of dielectric and impedance properties of SBT sample shows multiple relaxation behaviour. Relaxation times obtained from impedance and modulus plots appear to follow Arrhenius relation. A double well potential barrier model is used to understand the results.

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References