Impedance analysis of Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ ferroelectric ceramic

S RACHNA$^1$, SURYA M GUPTA$^1$ and S BHATTACHARYYA$^2$∗

$^1$Laser Materials Development and Devices Division, Raja Ramanna Centre for Advanced Technology, Indore 452 013, India
$^2$Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, USA

∗Corresponding author. E-mail: sudipto_iisc@yahoo.com

MS received 26 September 2006; revised 20 November 2007; accepted 4 March 2008

Abstract. AC impedance spectroscopy technique has been used to study electrical properties of Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ (BLT) ceramic. Complex impedance plots were fitted with three depressed semicircles, which are attributed to crystalline layer, plate boundary and grain boundary and all three were found to comprise of universal capacitance nature [C = $C_0 w^{-n-1}$]. Grain boundary resistance and capacitance evaluated from complex impedance plots have larger values than that of plate boundary and crystalline layer. The activation energies ($E_a$) for DC-conductance in grain boundary, plate boundary and crystalline layer are 0.68 eV, 0.89 eV and 0.89 eV, respectively. Relaxation activation energies calculated from impedance plots showed similar values, 0.81 eV and 0.80 eV for crystalline layer and plate boundary, respectively. These activation energy values are found to be consistent with the $E_a$ value of oxygen vacancies in perovskite materials. A mechanism is offered to explain the generation of oxygen vacancies in BLT ceramic and its role in temperature dependence of DC-conductance study.

Keywords. Ferroelectric memories; impedance; Bi-layered structure; oxygen ion-jump.

PACS Nos 84.37.+q; 77.84.-S; 85.50.Gk; 82.45.Xy; 77.84.Lf

1. Introduction

La-doped bismuth titanate (BLT) is a promising material for ferroelectric random access memory (FRAM), because of its low processing temperature and polarization retention up to $10^{10}$ switch cycles on Pt-electrodes [1,2].

Bismuth titanate (BT) is a layered structure ferroelectric, which belongs to the Aurivillius family of compounds [3]. The general formula of BT can be written as (Bi$_2$O$_2$)$_2^{2+}$(A$_{m-1}$B$_m$O$_{3m+1}$)$_{2-}$, where A is Bi$^{3+}$, B is Ti$^{4+}$ and $m = 3$ [4–6]. Thus, the stoichiometric composition is Bi$_4$Ti$_3$O$_{12}$. The unit cell consists of alternating layers of (Bi$_2$O$_2$)$_2^{2+}$ and three pseudo-perovskite layers of oxygen octahedra of (Bi$_2$Ti$_3$O$_{10}$)$_{2-}$ stacked in the c-direction [7,8]. The polarization direction is in
the $ab$-plane at $4.5^\circ$ to $a$-axis [9–11]. The plate-like grain morphology gives rise to electrical anisotropy with the higher component of its spontaneous polarization ($P_S = 50 \mu C/cm^2$) parallel to the bismuth layers [12–14]. Recently, impedance spectroscopy of BLT ceramics has been reported [15] in which the complex impedance spectra above $250^\circ C$ were fitted by assuming an equivalent circuit comprising of the contributions of grain and grain boundaries. The experimental data were shown to fit remarkably up to $360^\circ C$. Above the transition temperature ($>400^\circ C$), the fitted low frequency data were found to deviate from the experimental data. It has already been reported [12] that a single crystal of BT consists of mica-like aspects when observed under scanning electron microscope. The impedance spectroscopy revealed two depressed semicircles. The depressed semicircle at low frequency was assigned to the plate boundary and the second depressed semicircle at high frequency was corresponding to bulk. The plate boundaries were present in the crystal and thus three semicircles are expected in the AC-impedance results of BLT ceramics. In view of this we have carried out impedance studies on BLT, with the aim to investigate the true picture of the electrical properties and its correlation with the sample microstructure. The results are fitted with a series addition of three depressed semicircles corresponding to grain and two barriers (i) plate and (ii) grain boundary.

2. Experimental details

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramic was prepared using the conventional solid-state reaction route. Stoichiometric amounts of high purity starting reagents $Bi_2O_3$, $La_2O_3$ and $TiO_2$ were mixed thoroughly with acetone and then ball-milled for 18 h. The slurry was dried at $80^\circ C$ and the powder was calcined at $800^\circ C$ for 4 h. Single phase formation of BLT pseudo-orthorhombic phase was confirmed by X-ray diffraction (XRD). The calcined powder was ball-milled again with acetone for 12 h. After drying, the powder was pressed into cylinders using polyvinyl alcohol (PVA) as a binder and a uniaxial hydrostatic pressure of 120 MPa. These cylinders were fired at $1100^\circ C$ for 2 h after binder burnout at $450^\circ C$ for 4 h. These cylinders were fired under covered alumina crucible, and a small amount of $Bi_2O_3$ powder was placed near the sample in order to minimize bismuth oxide loss. All sintered pellets had a final density greater than 98% of the theoretical value. The calcined and sintered specimens were analysed by Rigaku X-ray diffractometer, operated at 30 KV and 20 mA, using CuK$_\alpha$ radiation for second phase formation. The sintered blocks were then cut into thin disks and polished on different grades of emery papers to obtain parallel surfaces. The polished surfaces were ultrasonically cleaned to remove dust particles. Sample discs using a thin coating of high temperature drying silver paste (cured at $500^\circ C$ for two hours in air) were used as electrodes to ensure good electrical contact.

The dielectric response was measured using a Hewlett-Packard 4194A impedance analyzer which can cover a frequency range of 100 to $15 \times 10^6$ Hz. For high temperature measurements, the samples were placed in a custom-built tube furnace, which can be operated between 30 and $800^\circ C$. The temperature was measured using a Eurotherm controller 800 via a K-type thermocouple mounted directly on the
Impedance analysis of Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$

Figure 1. X-ray diffraction pattern of sintered Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ ceramic at room temperature.

insulation (alumina) of the ground electrode of the sample fixture. The impedance analyzer and Eurotherm controller were interfaced with computer to collect data while cooling as well as heating at a rate of 2°C/min.

Impedance measurement was carried out using HP 4194A impedance analyzer over a frequency range of 100 Hz to 1 MHz, at different temperatures (up to 500°C). The temperature was held constant for 10–15 min to obtain equilibrium. Impedance results were analysed using commercially available Z-View software [16].

3. Results and discussion

3.1 Phase and microstructural studies

Figure 1 shows X-ray diffraction pattern of Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ ceramic. All the major diffraction peaks were indexed with pure Bi$_4$Ti$_3$O$_{12}$ orthorhombic phase. No peak corresponding to pyrochlore and fluorite type was detected. Lattice parameters $a = 5.42$ Å, $b = 5.41$ Å, $c = 32.89$ Å and $\alpha$, $\beta$, $\gamma = 90^\circ$ were determined.

Scanning electron micrograph of the fractured surface of the sintered specimen is shown in figure 2. Well-developed plate-like grains with average grain size of ~5 μm in length and ~2 μm in width could be seen. Similar plate-like grain morphology has already been reported for BLT sintered ceramic [17]. The sintered density was measured using the Archimedes principle and 98% of the theoretical density was measured.
3.2 Impedance and dielectric analysis

Figure 3a shows the temperature dependence of real dielectric constant at different frequencies. The Curie temperature $T_c$ was obtained from the peak value of the temperature dependence of dielectric constant plot. $T_c$ was estimated to be 400°C at 1 MHz frequency and that is consistent with the reported value [18]. Strong frequency dispersion was observed for BLT ceramic with increasing temperature. High conducting losses masks the peak corresponding to phase transition at all frequency (<100 kHz) in temperature dependence of dielectric constant plot. Figure 3b shows the variation of dissipation factor with temperature at various frequencies. A low frequency tan δ peak was observed between 150°C and 300°C temperature range. According to Debye model, reciprocal frequency of each peak gives relaxation time $\tau$ (in sec). When relaxation time versus reciprocal of peak temperature is plotted, a straight line is observed (inset of figure 3b). The plot is fitted with the Arrhenius relationship, where slope is equal to the activation energy ($E_a$), as shown in eq. (1):

$$\tau = \tau_0 \exp(-E_a/k_BT), \tag{1}$$

where $\tau_0$ is the time constant, $k$ is the Boltzmann’s constant and $T$ is the temperature at which the relaxation peak is maximum.

Relaxation activation energy 0.87 eV with time constant $\tau_0 = 7.86e^{-12}$ s was calculated. These parameters are indicative of ion-jump or dipole relaxation [19,20]. An oxygen ion hopping has been proposed to attribute the relaxation observed in this temperature regime [21].

Figures 4a,b show the variation of real and imaginary impedance ($Z'$ and $Z''$) with frequency at different temperatures. The $Z'$ value was found to decrease with increasing frequency at all temperatures. The $Z''$ also decreased with increasing
Impedance analysis of $Bi_{1.25}La_{0.75}Ti_3O_{12}$

Figure 3. Dependence of (a) $\varepsilon'$ and (b) $\tan \delta$ on temperature for frequencies ranging from 100 Hz to 1 MHz. (Inset of figure 3b shows variation of relaxation time with inverse of temperature.)

Temperature, which is due to an increase in the conducting losses. The frequency corresponding to $Z''_{\text{max}}$ shifted to higher values with increasing temperature. The peak height for both the peaks (figure 4b) was decreased with increase of temperature indicating an increase in the conducting loss.

Figures 5a, b show complex impedance plots for temperatures 250°C and 500°C, respectively. The complex impedance plot obtained at all temperatures is compared in figure 6. Recently, the complex impedance plots were resolved with two depressed semicircles corresponding to grain and grain boundaries [15]. Spectroscopic plots measured below and above $T_c$ were fitted by superposition of two Cole–Cole expressions:
Figure 4. Spectroscopic (a) real and (b) imaginary part of impedance ($Z'$) plots of BLT in the temperature range 325°C–475°C. Solid lines are fitting results with the proposed equivalent circuit presented in figure 5a.

\[ Z' = \frac{R_1}{1 + (i\omega\tau_1)^m} + \frac{R_2}{1 + (i\omega\tau_2)^n}, \]

where $R_1$, $R_2$, $\tau_1$ and $\tau_2$ are resistances and relaxation times for grain and grain boundaries, respectively. The above equation was reported to fit well with the spectroscopic plots of BLT below $T_c$ but strong deviation could be seen in low frequency regime above $T_c$. The proposed equivalent circuit [15] was also used to fit our experimental data. The inset of figure 5b shows the fitting of experimental data at 500°C with eq. (2). It should be noticed that the experimental data of low frequency does not match properly, as marked by arrows. These experimental plots were fitted by equivalent circuit model as shown in figure 5a. The experimental plots were completely resolved into three depressed semicircles, i.e. semicircle centred...
Impedance analysis of $Bi_{1.25}La_{0.75}Ti_3O_{12}$

Figure 5. Experimental, simulated, theoretical and deconvoluted complex impedance plots of BLT at (a) 250°C and (b) 500°C. Series addition of 3RQ-type equivalent circuit used for fitting experimental data is shown. Inset of figure 5b shows fitting of experimental data at 500°C assuming 2RQ.

below the abscissa axis, suggests the relaxation to be of non-Debye type. The solid line in figures 4a, b and 6 is the fitting of the experimental data by the equivalent circuit as shown in figure 5a. Excellent fitting of experimental data with the proposed equivalent circuit may be noticed.

Considering complex impedance plots of BT single crystal and ceramic as reported by Huanosta et al [17] and Macedo et al [22], respectively, low, intermediate and high frequency arcs were ascribed to grain boundary, plate boundary and crystalline layer, respectively. Each depressed semicircle is represented by parallel resistance-constant phase element (RQ) circuit. The constant phase element (CPE) is expressed by eq. (3) and defined by two values, $C_0$ and $n$ [23–25],

\[ C = C_0(j\omega)^{n-1}, \]  

(3)
S Rachna, Surya M Gupta and S Bhattacharyya

Figure 6. Nyquist diagram of the sintered BLT ceramic above and below (inset) the transition temperature. The temperature is marked in the respective plot. Fitting results using 3RCPE-type equivalent circuit is shown by solid line.

where $C_0$ is expressed in units of capacitance component and $\omega$ is the angular frequency ($=2\pi f$). The CPE is identical to a capacitance component when the exponent $n = 1$, to a resistance component when $n = 0$, and to a Warburg component when $n = 0.5$. When CPE is placed parallel to a resistance, a Cole element (depressed semicircle) is produced.

The value of circuit parameters were estimated by nonlinear least square fitting with the aid of the program Z-view [15]. The capacitances ($C_{CL}$, $C_{PB}$, and $C_{GB}$) and exponent $n$ ($n_{CL}$, $n_{PB}$ and $n_{GB}$) due to crystalline layer, plate boundary and grain boundaries were obtained by fitting Nyquist plots at all temperatures. Figure 7 shows the temperature variation of $C_{CL}$, $C_{PB}$, $C_{GB}$, $n_{CL}$, $n_{PB}$ and $n_{GB}$ obtained from the Nyquist plots. A sudden change in capacitance of $C_{CL}$, $C_{PB}$, and $C_{GB}$ is attributed to ferroelectric transition at $T_c$. The capacitance of the crystalline layer was found to decrease above the transition temperature, which is consistent with the ferroelectric nature of the grain of BLT. An increase in $C_{PB}$ and $C_{GB}$ above $T_c$ may be due to the defect contribution in this temperature regime. From the temperature variation of $n$, $n_{GB}$ was found to decrease with increase of temperature below and above $T_c$, which depicts a clear departure from the ideal behaviour. Abnormal change in the value of $n_{CL}$, $n_{PB}$ and $n_{GB}$ at $T_c$ may be attributed to increase of disorder at $T_c$. Similarly, an abnormal change in the fitting parameters (coefficient $A$ and exponent $S$ from the power relation proposed by Jonscher) near the Curie temperature for ferromagnetic spinel (Zn$_{0.44}$Mn$_{0.56}$Fe$_2$O$_4$) and ferroelectric perovskite (Sr$_{0.25}$Bi$_4$Ti$_{3.25}$O$_{12.75}$) were attributed to an increase in the disorder near the phase transition [26].

Figure 8a shows the de-convoluted spectroscopic plots of three microstructural elements as well as the fitting curve along with the experimental data points. The relaxation time was calculated for each microstructural element at all temperatures.
Impedance analysis of Bi$_{1.25}$La$_{0.75}$Ti$_3$O$_{12}$

Figure 7. Comparison of temperature-dependent exponent $n$ and capacitance $C_0$ for the crystalline layer, plate boundary and grain boundaries.

below $T_c$. At the peak, the relaxation time $\tau_m$ is defined by eq. (4):

$$\omega_m \tau_m = 1,$$

where $\omega_m$ is the relaxation frequency. Figure 8b shows that the relaxation time obey the Arrhenius relation given by eq. (1). The activation energy, $E_a$, calculated from the plot of $\log \tau_m$ vs. $1/T$, is 0.81 eV and 0.80 eV for crystalline layer and plate boundary, respectively. A close resemblance of two values indicates that plate boundary and crystalline layer has the same type of relaxation processes. The activation energy values are in good agreement with the ion-jump mechanism [21]. The convoluted peak corresponding to the grain boundaries was quite broad, and so relaxation time for grain boundary could not be calculated.

The radius of deconvoluted arc in complex impedance is equal to electrical resistance of the microstructural region. The resistance of crystalline layer ($R_{CL}$), plate boundary ($R_{PL}$) and grain boundary ($R_{GB}$) were obtained at all temperatures from the fitting of the Nyquist plots. DC-resistance of bulk sample ($R_{bulk}$) was obtained from series addition of the DC-resistance of the individual microstructural elements. Figure 9 shows the temperature variation of inverse of $R_{CL}$, $R_{PB}$, $R_{GB}$, and $R_{bulk}$ below $T_c$. It can be seen that grain boundaries are more resistive than plate boundary and crystalline layer in the observed temperature range. Hence bulk resistance ($R_{bulk}$) is governed by grain boundaries. From figure 9, the activation energy for the DC-conductance of all three microstructural elements was calculated. The nature of conductance at various temperatures was almost linear and obeyed the Arrhenius relationship

$$\sigma_{DC} = \sigma_0 \exp(-E'_a/k_B T),$$

where $E'_a$ is the activation energy of conduction and $T$ is the absolute temperature. The values $E'_{CL} = 0.89 \pm 0.04$ eV, $E'_{PB} = 0.89 \pm 0.02$ eV, $E'_{GB} = 0.68 \pm 0.03$ eV and $E'_{bulk} = 0.73 \pm 0.02$ eV were calculated in the ferroelectric region. The activation energy for grain boundaries was lower than that of crystalline plate or plate
boundaries at all temperatures. The activation energy values reported here showed good correlation with the earlier reported activation values [13,17,27–29]. Value of $E_{CL}^′$ and $E_{PB}^′$ are consistent with the activation energy values calculated from the relaxation time ($\tau$) plot. Close resemblance of these values indicate that there is a single mechanism for the relaxation and conduction processes and this has been attributed to oxygen ion-jump. It may be noted that the activation energy reported [15] are lower than that reported here. This difference might be related to the unintentional minor variations of processing temperature and other parameters (both at the calcination as well as sintering stage). These minor variations can lead
Impedance analysis of Bi$_{1.25}$La$_{0.75}$Ti$_3$O$_{12}$

Figure 9. Comparison of temperature-dependent DC-conductance of bulk sample, crystalline layer, plate boundary and grain boundaries.

to small compositional changes and might act as unintentional doping which can modify the binding energy of oxygen vacancies through electrostatic screening [30]. It may be noted that the BLT sample was sintered at 1100°C, which is higher than the melting point of bismuth oxide (840°C). Bismuth loss during sintering will generate bismuth ion vacancies. To maintain the charge neutrality in the sample, oxygen vacancies are created adjacent to Bi-vacancies site [31]. It has also been reported [32] that the oxygen vacancies do interact with the domain walls and are believed to be responsible for the fatigue failure in the perovskite system. It is assumed that these oxygen vacancies are present near the domain and plate boundaries in the ferroelectric region of BLT ceramic. Similar activation energy for the crystalline layer and plate boundaries should be observed and the present study clearly strengthens the assumption.

4. Conclusions

Single phase BLT ceramic samples were prepared by conventional solid state route. Dielectric studies showed that prepared BLT is in ferroelectric nature with the Curie temperature $\sim$400°C at 1 MHz. Variation of dissipation factor with temperature and frequency indicated that low frequency dispersion observed in dielectric plots was due to oxygen ion-jump relaxation. Plate-like grain morphology was assumed to make a barrier and impedance spectroscopic results were fitted taking plate boundary contribution along with grain and grain boundary. Impedance analysis confirmed the presence of crystalline layer, plate boundary and grain boundary microstructural element contributions to the bulk impedance. The grain boundaries were found to be least conductive as compared to that of any other BLT’s microstructural element constituents. Hence total sample conductance was found to be governed by the grain boundary and that is consistent with the series
addition of resistances. Oxygen ion-jump process is believed to be responsible for the DC-conduction and dielectric relaxation present in the crystalline layer and plate boundary.

References