Analysis of Electric Transport Mechanism of Barium Titanate by Impedance Spectroscopy

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Keywords: Dielectric Properties, Impedance, Perovskite, Grains, Activation Energy, Hopping mechanism.

Abstract. Barium titanate (BTO) samples were prepared by nano milling based solid state reaction method. Dielectric behavior of BTO sample has been investigated by temperature dependent impedance spectroscopy. The impedance analysis of BTO samples confirms that hopping of electrons and defects coexisted in sample and contribution of grain and grain boundary to dielectric behavior is discussed. A single semicircular arc obtained by Nyquist plots whose radius decreased with increase in temperature illustrates the prominent role of grains. The activation energy of defects was calculated from Arrhenius plot. These defects may be due to oxygen vacancies and hopping between Ti^{+4} to Ti^{+3} ions.

Introduction

Dielectric ceramic is considered as significant material in the progress of microelectronic and microwave communication systems. In order to minimize the device size, it is necessary to have a material with high dielectric constant and a low-temperature coefficient of the permittivity. Thus, most research efforts have been moved towards perovskite structured materials because it has octahedral orientated cations such as Ti^{4+}, Nb^{5+} and Ta^{5+} on the B sites. These cations contain three types of polarization mechanisms such as electronic, ionic, and dipolar which is reason of high values of dielectric constant. Its general formula is ABO_3. Among these dielectric ceramics, Barium titanate (BTO) is an important functional material because of its piezoelectric and ferroelectric properties. It is widely used in various applications such as thermistors, dynamic random access memory (DRAM), actuators, sensors and multilayer ceramic capacitors (MLCC) [1-4]. Furthermore, the BTO has less toxic nature as compared to the other ceramic materials [5].

Various research groups worked on this material because it is appropriate for energy storage applications and their physical properties can be easily modified by controlling its particle size. In addition, particle size determines the electrical resistance of the material. It is interesting to study the change in dielectric properties by particle size. To control the particle size, nano-ball milling based solid-state is suitable method because it is simple, fast and cost effective method. In the ball milling, the grinding bowl, straddling on a turning support frame, also revolves about its axis. The forces produced by these rotations are applied to the milling balls and materials inside the bowl. Particle size decreased and produce microstrains at the same time in the material due to these forces.

We have previously reported structural and dielectric properties of BTO at room temperature with different milling frequencies [6]. To understand the role of grain and grain boundary in different mechanisms such as polarization, conductivity and relaxation process, BTO sample was prepared using optimized parameters of the previous work. In the present work, dielectric measurements were performed at different temperatures. The behavior of dielectric constant, tangent loss and AC conductivity are discussed at all temperatures and associated with different polarization and conduction mechanism. The contribution of grain is analyzed using impedance spectroscopy. The values of activation energies were calculated at different frequencies by means of Arrhenius plot and correlated with structural defects.

Experimental Details

Barium titanate was prepared by solid state reaction. A mixture of BaO (99.99% pure, Sigma-Aldrich) and TiO$_2$ (99.99%, Merck) was prepared at room temperature.

$$BaO + TiO_2 \rightarrow BaTiO_3 \tag{1}$$

The mixture was ball milled [Fritsch, Germany] with five rotating balls at 50 Hz milling frequency for two hours in a ceramic bowl. Then pellet was prepared a using hydraulic press by applying pressure 27.58 MPa for 2 minutes. Area and thickness of pellet were 0.832 cm^2 and 0.185 cm, respectively. Afterwards, the samples were heated at 1200 °C in oxidizing environment for 24 hours. The Impedance analyzer (Wayne Kerr 6500 B) was used to determine the frequency dependent dielectric parameters at different temperatures (30 °C to 210 °C).

Results and Discussion

The Fig. 1 shows the temperature dependence of the dielectric constant at different frequencies. It is clear that the dielectric constant increases with increase in temperature. This increase in dielectric values can be attributed to the formation of insulating layer around the grains at high temperature. This layer is more resistive as compared to the grain [7]. The change in resistivity of grain (bulk) and layer (grain boundary) gives rise to the accumulation of charges which in turn results in the increase of internal polarization. Consequently, high dielectric value is observed at elevated temperatures. In addition, dielectric constant decreases as frequency is increased. Dielectric values decrease due to polarization. It can be explained as: there are four types (dipolar, electronic, ionic and interfacial) of polarization in dielectric materials. All the polarizations fully contribute to the applied electric field at low frequencies, whereas at high frequency response of different polarizations to the applied electric field becomes low leading to decrease in net polarization which reduces the dielectric values [8, 9]. Temperature dependent tangent loss for BTO samples is shown in Fig. 2. Similar to dielectric constant, tangent loss also has large dispersion at low frequencies because the charge carriers require more energy to flow due to resistive behavior of grain boundaries which increases the energy losses in the low frequencies region.

The impedance analysis of BTO has been reported in the literature [10-12]. However, the difference lies in dielectric parameters from one report to the other often ascribed the different techniques. This variation is due to the effects of grain size, chemical inhomogeneity, grain and grain boundary impedance. Thus, complex impedance spectroscopy is suitable method to investigate the electrical behavior of ceramic materials and their temperature dependence. In order to analyze the electric properties, it is necessary to understand how the dielectric data transforms according to different formalism. The Z is suitable function to explore the resistive and/or conductive behavior of material. Fig. 3 shows the Nyquist plots of BTO at different temperatures. The data obtained at room temperature illustrates a straight line (not shown here) with large slope indicating the insulating behavior of BTO at room temperature. The slope reduced with the increase in temperature and semicircular arcs are formed by bending the slope towards the major (Z) axis. As the temperature is increased, the radius of curvature decreased, which indicate the conducting nature at high temperature. However, the presence of a single semicircular arc indicates the grain interior (bulk) property of the material [13]. It is observed that the magnitude of Z' decreases with increase in temperature, which can be related to the increase in AC conductivity in the specimen. It is possible that defects such as oxygen vacancies result in the increase of AC conductivity. Thus, the role of oxygen vacancies is dominant at high temperature, whereas these defects are immobile at low temperature. The variation in the highest value of Z" is due to the presence of temperature dependent relaxation process.
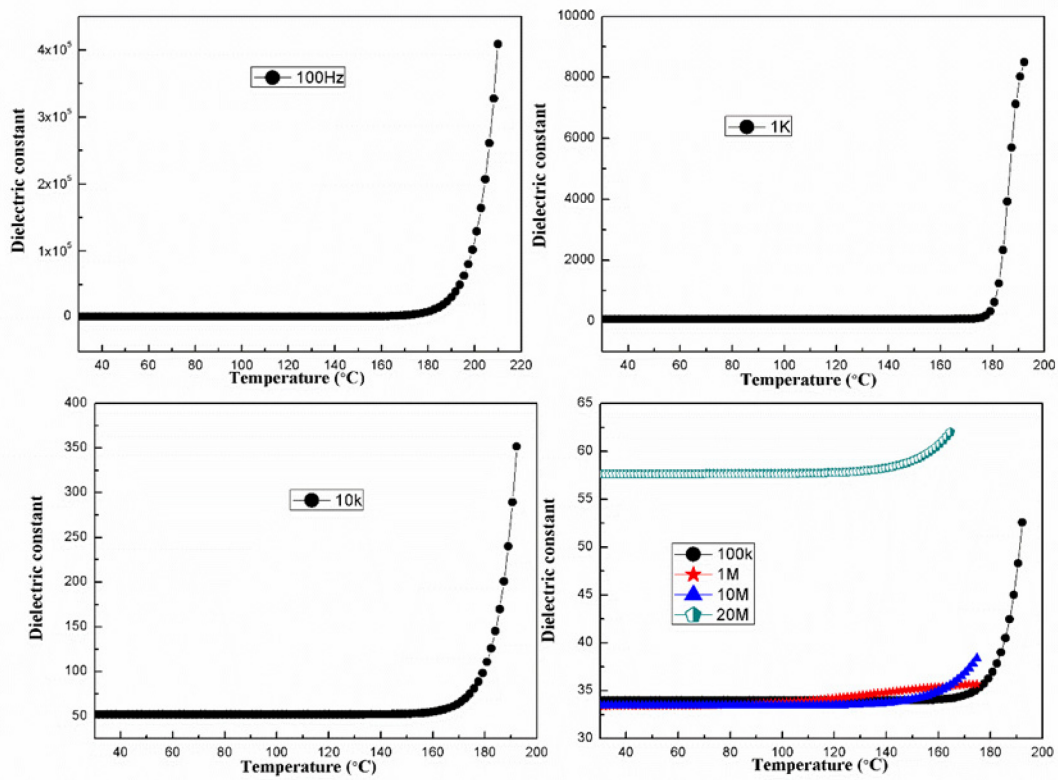
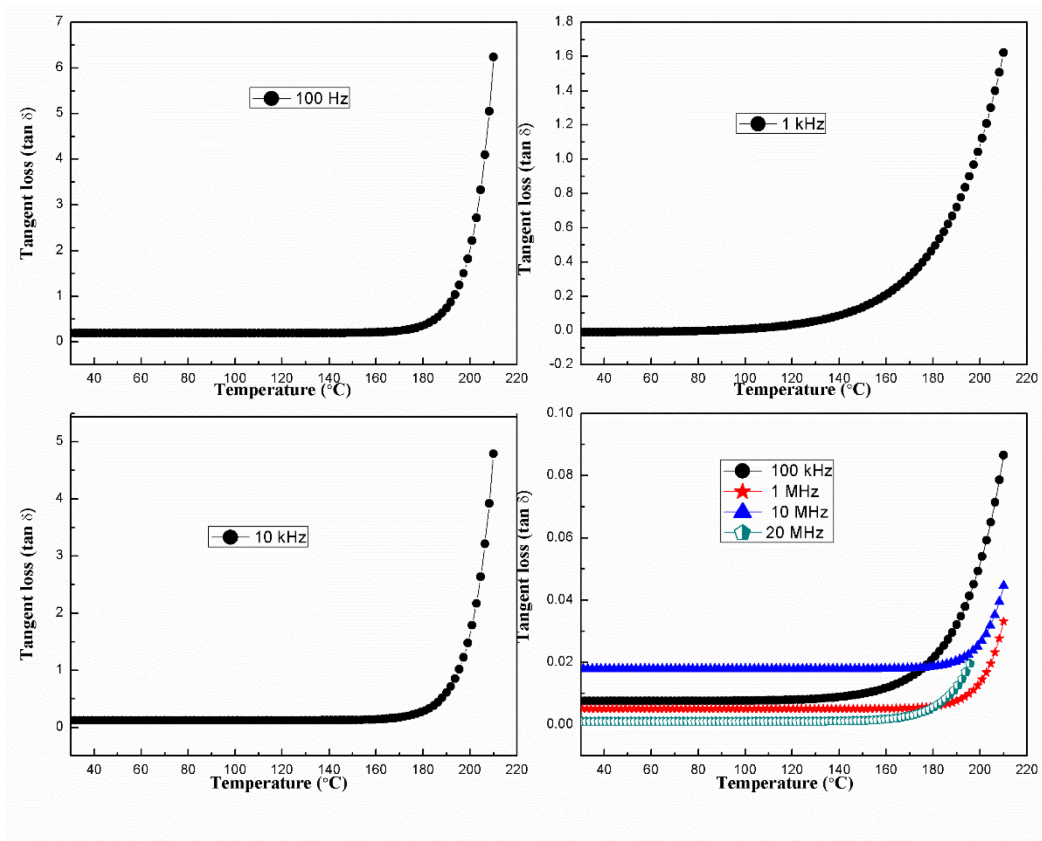Fig. 1 Dielectric constant of BTO at various frequencies from100 Hz to 20MHz.

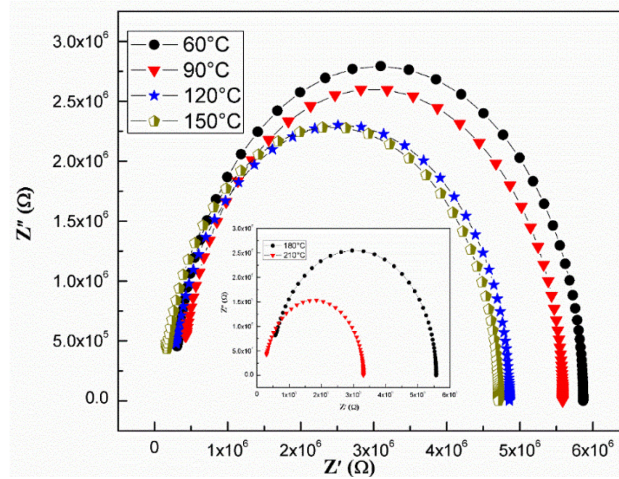Fig. 2 Tangent loss of BTO at various frequencies from100 Hz to 20MHz.

Fig. 3 Nyquist plots of BTO ceramics at different temperatures.

Fig. 4 demonstrates the variation of AC conductivity (σ_{ac}) with frequency at different temperatures from 30 °C to 210 °C which reveals that AC conductivity strongly depends on the frequency. The conductivity depends on the lattice defects in solids such as vacancies and dislocations as reported in previous studies [14,15]. There is a gradual increase in AC conductivity with increase in frequency of applied field due to the increase in hopping of electrons between ions. Furthermore, lattice defects can influence the motion of charges resulting in changed conductivity. The presence of Ti^{3+} ions and oxygen vacancies is responsible for hopping mechanism in BTO [16]. It is observed that the AC conductivity increased with increase in temperature. The increase in conductivity with temperature results in an increase in drift mobility of the charge carriers, which enhances the hopping mechanism [17]. The electrical conduction improvement at high temperature supports the impedance analysis results.

The plots of AC conductivity as a function of temperatures is shown in Fig. 5. It is clear from the figure that there are two regions which indicate the presence of different conduction mechanisms. Every region has its different activation energy at a particular frequency. The values of the activation energy of two regions at different frequencies were calculated according to the Arrhenius law [18].
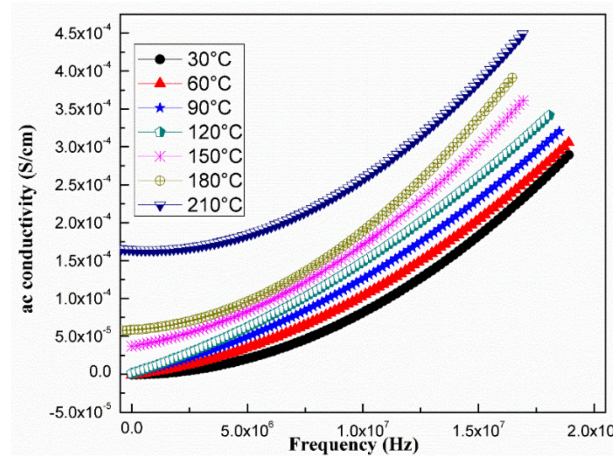

Fig. 4 Variation of AC conductivity vs. frequency at various temperatures.

$$\sigma_{ac} = \sigma_0 exp\left(-\frac{E_a}{k_B T}\right) \tag{2}$$

Where, σ_0, σ_{ac}, E_a, k_B and T are pre-exponential term, AC conductivity, activation energy, Boltzmann constant and temperature in Kelvin scale, respectively
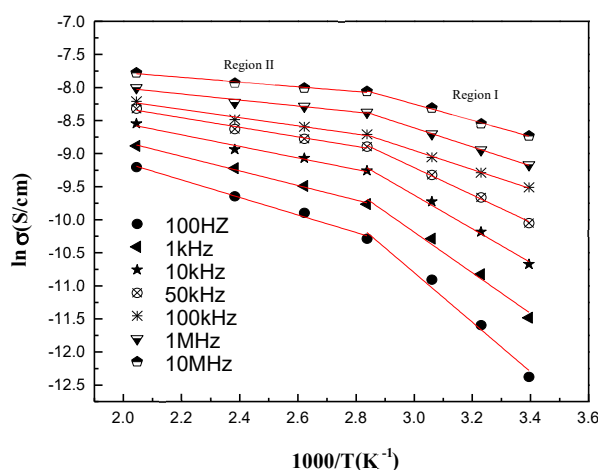
Fig. 5 Variation of AC conductivity vs. inverse of temperature at different frequencies for BTO.

The calculated values of the activation energy at various frequencies are given in Table 1.

Table 1 Activation energy values (E_a) for AC conduction calculated by Arrhenius plots for both regions indicated in Fig. 5 at various frequencies.

f(Hz)	E(meV) of region I	E(meV) of region II
100	323	114
1k	265	95
10k	219	75
50k	178	62
100k	124	54
1M	124	39
10M	106	31

The values of activation energy at various frequencies increase in region-I as compared with region-II. The interaction between electron and/or hole-phonon enhances at low temperature due to the lattice deformation. This lattice deformation can be due to the presence of Ti^{3+} ions and oxygen vacancies. The induction of small polarons due to interaction between electron and/or hole-phonon is the reason for high value of activation energy. At high temperature, values of activation energy are found to vary from 31 to 114 meV. The activation energy in this region is associated with the hopping charge mechanism related with oxidation and reduction process. Furthermore, oxygen vacancies exhibit more mobility at high temperature and become activated to contribute in conduction process. The calculated values of energy are consistent with double ionized oxygen vacancies present in ceramic oxides described in literature for various ceramic oxides associated with hopping mechanism [19].

Conclusions

Barium titanate ceramic sample has been synthesized by nano-milling based solid state reaction technique. Frequency dependent dielectric measurements at different temperatures has been performed. Dielectric constant, tangent loss, AC conductivity and impedance analysis point out the relationship between temperature and microstructure effect which can be explained on the basis of Koop's theory. The contribution of grain (bulk) is observed in the material by Impedance spectroscopy using Nyquist plots. The mobility of the structural defects through hopping is the origin of electrical conduction in BTO. The activation energy values of these defects were calculated by Arrhenius plots. Highest activation energy value at low frequency indicated the dominant role of grains at high frequency.

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