Structural and Electrical Properties of BaTiO₃ prepared by Solid State Route

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Abstract

Barium titanate (BaTiO₃) sample was prepared by the standard solid state reaction method and was sintered at 1200 ^{o}C for 12 hours. The X-ray diffraction result confirms the formation of BaTiO₃ phase with tetragonal structure. Scanning electron microscope (SEM) observations revealed microstructural uniformity with average grain size in the range of 2.71µm. The temperature dependent dielectric constant showed a transition temperature at around 140 ^{o}C. The dielectric constant and loss factor was found to decrease with an increase in frequency and it became independent at higher frequency range. The variation of dc resistivity with temperature showed ohmic behavior. As the temperature increased the dc resistivity of the sample is decreased. The activation energy also changed at transition from ferroelectric to paraelectric state.

Keywords: X-ray Diffraction; SEM; Dielectric constant; Dielectric loss and dc resistivity.

Introduction

A number of physicists have proposed model theories of ferroelectricity. Mason and Matthias in 1948 proposed the model theory for BaTiO₃ crystal [1]. They have suggested that Ti^{4+} ions are mainly responsible for ferroelectric properties of BaTiO₃. Experimental capabilities now allow layer-by-layer epitaxial growth of perovskite-based oxides, facilitating the exploration of a wide range of artificial materials inaccessible by conventional solid-state synthesis. Barium titanate (BaTiO₃) is a ferroelectric oxide that undergoes a transition from a ferroelectric tetragonal phase to a paraelectric cubic phase upon heating above 130 °C. In cubic perovskite BaTiO₃, titanium atoms are octahedrally coordinated by six oxygen atoms. Ferroelectricity in tetragonal BaTiO₃ arises due to an average relative displacement along the c-axis of titanium from its centrosymmetric position in the unit cell and consequently the creation of a permanent electric dipole. The elongation of the unit cell along the c-axis and consequently the deviation of the c/a ratio from unity are used as an indication of the presence of the ferroelectric phase [2-5]. BaTiO₃ is particularly challenging since it exhibits three solid-solid phase transitions. The high dielectric permittivity combined with low dissipation factor makes one of the promising candidates for dynamic random access memory, decoupling capacitors, and dielectric field tunable elements for high frequency device applications [2].

In this paper, we focus on synthesis and study of electrical properties BaTiO₃ which is an important member of the family of ferroelectric perovskites.

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Experimental Work

Synthesis of powders

$BaTiO_3$ was prepared through solid solution reaction by standard double sintering ceramic technique using AR grade $BaCO_3$ and TiO_2. The raw powders were thoroughly mixed in agate mortar and the homogeneous mixtures were presintered at 1000 ^{o}C for 10 hrs. After presintering it was ground to fine powders and then mixed with 2 % polyvinyl alcohol as a binder as a binder and pressed into pellets of 15 mm diameter and thickness of 1.96 mm using a hydraulic press. The pelletized samples were finally sintered at 1200 ^{o}C for 12 hrs in a programmable furnace.

Physical Characterization

The X-ray diffraction patterns of samples were taken by using Phillips X-ray diffractometer (Model PW-1710) using CuK_α radiation (λ = 1.5418 Å). The particle morphological features were imaged by scanning electron microscopy (SEM, JEOL JSM 6360) with an accelerating voltage of 25 kV.

Electric Measurements

The silver paste was applied on the flat surfaces of the pellets for good electrical contacts. The dc resistivity measurements were made by two probe method in the temperature range from room temperature to 300 - 500 ^{o}C. For measurements of dc resistivity a constant voltage of 2 V was applied across the sample through a transistorized power supply unit (TPSU) and the current was measured at different temperature using a digital nanometer. The resistivity was calculated by using standard relation. The AC parameters such as capacitance (c) and dissipation factor (tan δ) of the samples were measured in the frequency range 100 Hz - 1 MHz using LCR meter bridge (HP Model 4284 A). The variation of dielectric constant and loss tangent with temperature at different frequencies was also measured. The dielectric constant was calculated by using relation,

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$

--- (1)

where, c is a capacitance of the pellet in Farad, d the thickness of the pellet (~ 1.96 mm) and A is the area of the pellet with diameter ~ 14.94 mm.

Results and Discussions

Figure 1 shows the X-ray diffraction pattern of $BaTiO_3$ ferroelectric. The pattern shows well defined peaks and there is no any intermediate phase is formed, confirming the single phase formation of $BaTiO_3$. The occurrence of splitting of peaks with specific indices characteristic indicates the tetragonal perovskite structure in the $BaTiO_3$ ferroelectric phase. The lattice parameters are found to be a = 3.98 Å and c = 4.04 Å with c/a = 1.015. This suggests that the crystal structure is tetragonal at room temperature.

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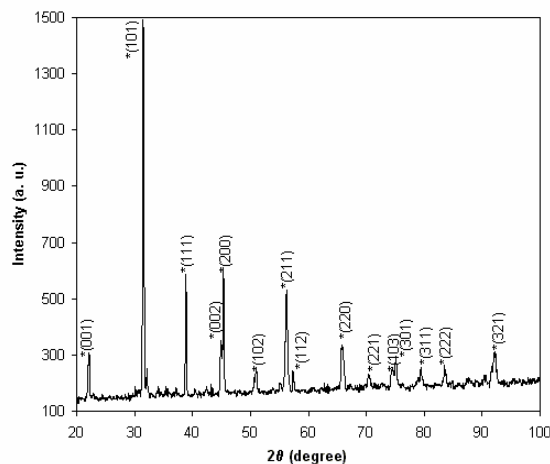The calculated and observed 'd' values are in good agreement for all indexed planes.

Figure 1. X-ray diffraction pattern of as sintered BaTiO$_3$

The particle size was calculated by using the Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$ --- (2)

where, 0.9 is the shape factor, λ is the X-ray wavelength i.e. 15.4178 nm, β is the line broadening at half the maximum intensity (FWHM) in radians and θ is the Bragg angle [6].

The average particle size was found to be around 46 nm. Moreover, the X-ray density, actual density and % of porosity of BaTiO$_3$ ferroelectric phase were found to be 6.03, 4.76 and 21.17 % respectively. The SEM microphotograph for ferroelectric BaTiO$_3$ is shown in Figure 2. Pore free uniform grains can be seen from the surface micrographs of BaTiO$_3$ samples. The shapes of the grains are spherical on an average. The average grain size of 2.71 µm, estimated by the linear intercept method is observed for sintered BaTiO$_3$ samples.
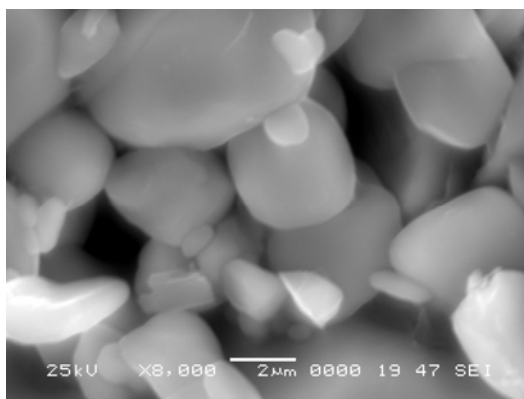

Figure 2. SEM micrographs ferroelectric (BaTiO$_3$)

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The variation of dielectric constant (ε) with temperature at different frequencies viz. 1 kHz, 10 kHz, 100 kHz and 1 MHz for the $BaTiO_3$ phase is shown in Figure 3. It can be seen that like any normal ferroelectric the dielectric constant at any frequency increases gradually with rise in temperature up to its maximum value at Curie temperature (Tc) and then it decreases, indicating the phase transition from ferroelectric state to paraelectric state at Curie temperature (Tc). Dielectric constant (ε) of any material, in general, is influenced by dipolar, electronic, ionic and interfacial polarizations. Interfacial polarization increases due to the creation of crystal defects and dipolar polarization decreases due to the increase in randomness of the dipoles with temperature. However, the temperature effect on ionic and electronic polarizations is very small. The increase in ε with temperature suggests the increase in interfacial polarization in this material. The maximum dielectric constant is observed at the ferroelectric to paraelectric phase transition (Curie point T_c). At Tc electrons are thermally activated, an increase in temperature results in increase dielectric polarization, which in turn causes an increase in dielectric constant. Curie point T_c, is dependant on tetragonality ratio c/a, means crystallite size and crystal lattice microstrain. After certain critical values of tetragonality ratio c/a, crystallite size and crystal lattice microstrain decreases. A possible explanation for this behavior of the $BaTiO_3$, Curie point is based on differences in free energy of the paraelectric and ferroelectric states. It is well known that the tetragonal (ferroelectric) state has a lower free energy than the cubic (paraelectric) $BaTiO_3$ state. A recently developed theory concerned with the part of the free energy related to the polarization shows that small crystallites (mostly single domained) have large depolarization energy. Because of that, the total free energy has a higher value.
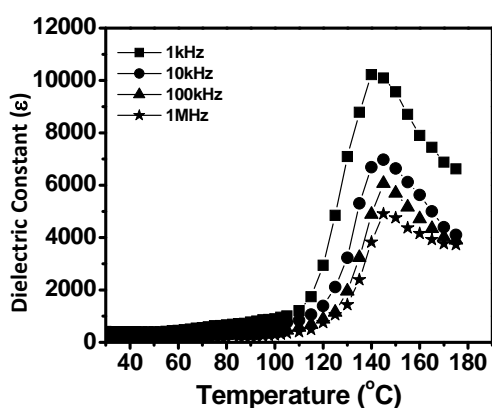

Figure 3. The variation of dielectric constant (ε) with temperature at different frequencies for sintered $BaTiO_3$
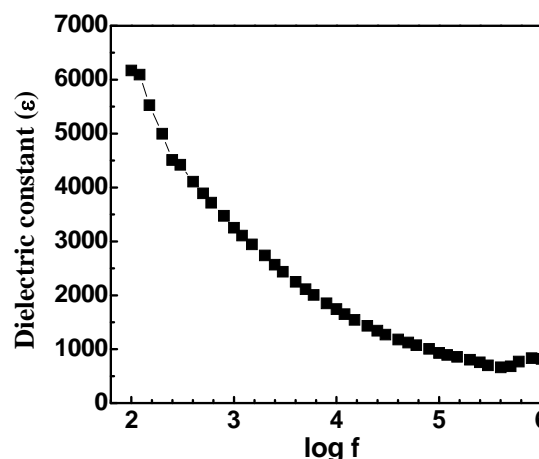

Figure 4. Variation of dielectric constant with frequency for $BaTiO_3$ ceramic

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The multidomain structures of the larger crystallites, on the other hand, reduce the depolarization energy and thus the total free energy has lower value and the tetragonal structure is stable. Increase of total free energy resulted in a less stable tetragonal $BaTiO_3$ state compared with cubic state [7]. A maximum value of dielectric constant of sintered $BaTiO_3$ samples is found to be 10221 at Curie temperature. The variations of dielectric constant and dielectric loss with frequency are shown in Figures 4 and 5 respectively.

The dielectric constant decreases with increase in frequency showing dispersion in the lower frequency range. The high values of dielectric constant observed at low frequencies are explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The in-homogeneities in the present system are impurities, porosity and grain structure. In weak external field, sample behaves as a linear dielectric because the associated domains do not participate in the polarization [8]. According to Rezlescu [9], the dielectric behavior in the material is due to the collective contribution of two types of carriers p and n to the polarization. The behavior is relaxor type. The high permitivities observed in the lower frequency is not usually intrinsic but are rather associated with a heterogeneous conduction.
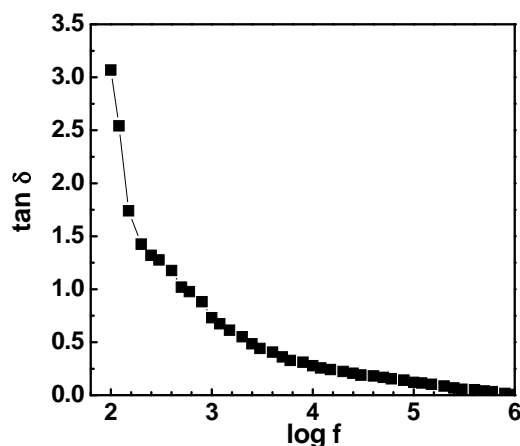

Figure 5. Variation of dielectric loss with frequency for $BaTiO_3$ ceramic

The response time $1/\omega_{max}$ of the interfacial polarization compared with other mechanism is relatively long that observe dielectric relaxation and larger interfacial polarization at a lower frequency [10]. Many workers [11] have studied the variation of dielectric constant with frequency. They have explained that the mechanism of dielectric polarisation is similar to that of conduction. In normal dielectric behaviour, ε decreases with frequency and reaches a constant value at higher frequencies. The variation of dielectric loss (tan δ) with frequency at room temperature of $BaTiO_3$ is similar to that of dispersion of dielectric constant. At low frequency, the tan δ value was observed to be large and it decreases with increasing frequency. The physical significance of tanδ is the energy dissipation in the dielectric system, which is proportional to the imaginary part (ε'') of dielectric constant. Similar results

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have been reported by various worker [12-13]. The Figure 6 shows the varaiation of resistivity with tempearture for sintered $BaTiO_3$ ferroelectric. The resistivity decreases with increasing temperature. The samples indicate the semiconducting nature. However, the break is observed in the linear variation at Curie temperature (= 150 ^oC). There are two regions in the resistivity plot. The first region observed at lower temperatures is due to impurities and may be attributed to the ordered state of ferroelectric phase and the second region that occurs at higher temperature which is due to polaron hopping may be attributed to disordered paraelectric state. It is also observed that the rate of decrease of resistivity is slow up to the transition temperature and there after it decreases rapidly. The dc activation energies, E_{dc} , in the ferroelectric and paraelectric region have been calculated using the Arrhenius equation

$$\rho_{dc} = \rho_0 \, exp\frac{E_{dc}}{k_B T}$$ --- (3)

where, k_B is the Boltzmann constant. There is change in activation energy when transition from ferroelectric to paraelectric state takes place. The activation energy found in ferroelectric state is 0.05 eV and in paraelectric state it is 0.38 eV. The reported value of activation E_{dc} for $BaTiO_3$ is 0.07 eV [14]. These values of E_{dc} suggest electronic type conduction in these materials. The conduction is due to large effective mass and low mobility of current carriers. The lowering of the activation energy is attributed to the effect of spin ordering.
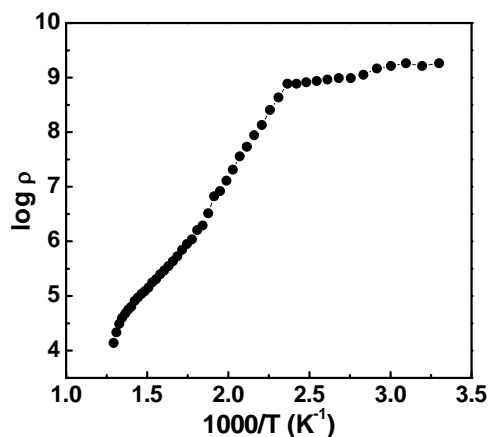

Figure 6. Variation of dc resistivity with temperature for $BaTiO_3$ ceramics.

Conclusions

The $BaTiO_3$ ferroelectric was preparde by the standard double sintering ceramic method. The XRD pattern of the $BaTiO_3$ confirm tetragonal perovskite phase formation. The average grain size of the sintered $BaTiO_3$ is found to be 2.71 μm. The phase transition from ferroelectric to paraelectric is observed at Curie temperature. The maximum value of dielectric constant is observed at Curie temperature. The dielectric constant decreases with increase in frequency showing dispersion in the lower frequency range.

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The resistivity decreases with increasing temperature, which indicates the semiconducting nature of the sample.

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