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# Ac conductivity and relaxation mechanism in $Ba_{0.9}Sr_{0.1}TiO_3$

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ABSTRACT

The ac conductivity and relaxation mechanism in $Ba_{0.9}Sr_{0.1}TiO_3$ ceramics have been investigated systematically. A high-temperature solid-state reaction technique was used to synthesize the compound. The formation of the compound was checked by an X-ray diffraction (XRD) technique. The dielectric permittivity and the loss tangent of the sample were measured in a frequency range from 1 kHz to 1 MHz at different temperatures (30–500 °C). A study on dielectric properties reveals the electrical relaxation phenomenon occurs in the material. The activation energy was calculated from the temperature variation of dc conductivity. Studies of frequency and temperature dependence of ac conductivity of the compound suggest that conduction process in the material is thermally activated.



## 1. Introduction

Inherent definition of ferroelectricity is the existence of a polarization state, the direction of which can be reversed by an externally applied electric field [1]. This property makes ferroelectric materials obvious candidates for new device applications [2,3]. Integration of ferroelectrics into electronic devices demands their use in the present era. Since the discovery of ferroelectricity in perovskite oxide material $BaTiO_3$ in 1945 [4], a large number of pure or complex ferroelectric oxides of different structural family have been examined for a wide variety of applications. For this, physical properties of the materials have been tailored by making suitable substitution in the materials or fabricating composites. Among them, barium titanate modified by Sr substitution at the Ba sites (i.e., $(Ba,Sr)TiO_3$) has emerged as a leading candidate due to its unique physical properties (i.e., high permittivity, low dielectric loss, better tunability, etc.), which makes it special for electronic applications such as multilayer and voltage tunable capacitors, infrared sensors, electro-optic devices, memories, etc. [5,6]. As it is well known, the tunability of a particular material shows how much the dielectric constant and other related proportion of the material can be changed upon an applied electric field and/or other experimental conditions. Further, the mentioned characteristics strongly depend on composition, raw materials, processing, microstructure, temperature, electric field, and frequency. There has been a considerable effort on improvement of some physical properties of perovskite-phase of $(Ba,Sr)TiO_3$ ceramics with proper selection of the Ba/Sr ratio. Such modifications were found to be greatly influenced the electrical properties [7] including leakage current [8], dielectric dispersion [9], and breakdown field strength [10]. $Ba_{0.9}Sr_{0.1}TiO_3$ (BST) ceramic possesses a very high degree of structural and compositional flexibility, due to their ability to accommodate a wide variety of cations on both the A and B sites [11,12]. Its lead free composition follows the environment. The frequency dependence of dielectric properties of the materials can be described in terms of complex permittivity ($\varepsilon_r^*$), complex conductivity ($\sigma^*$) and loss tangent ($\tan\delta$) and other related physical properties. These are written as follows: complex permittivity, $\varepsilon_r^* = \varepsilon' - j\varepsilon''$, complex conductivity, $\sigma^* = \sigma' - j\sigma''$, loss tangent, $\tan\delta = \varepsilon''/\varepsilon'$, $\sigma_{dc} = t/R_bA$ and $\sigma_{ac} = \varepsilon_0\varepsilon_r\omega\tan\delta$; where $j = \sqrt{-1}$, $\omega$ is $2\pi f$ (angular frequency), $C_0$ the geometrical capacitance of the sample, $\varepsilon_0$ the permittivity of the free space ($8.854 \times 10^{-12}$ F/m), $\sigma$ the conductivity, $R_b$ the bulk resistance, $t$ the thickness and $A$ area of the electrode deposited on the sample. Though synthesis and characterization of $(Ba,Sr)TiO_3$ on both bulk and thin films have been reported [13–15] in the literatures, detailed studies on the electrical, dielectric and impedance parameters with temperature and frequency, and its correlation with the microstructure in the studied sample, have not yet been reported. Therefore, in this article, we report the ac conductivity studies and relaxation mechanism in BST (Ba/Sr = 9:1) ceramics.

### 2. Experimental procedure

The polycrystalline samples of $Ba_{0.9}Sr_{0.1}TiO_3$ was prepared using a high-temperature solid-state reaction technique using high-purity (≥99.9%) carbonates and oxide; $BaCO_3$, $SrCO_3$ (M/S-Loba Chemie Pvt. Ltd.) and $TiO_2$ (M/S-S.D. fine). The above ingredients (carbonates and oxide) were mixed thoroughly in a desired sto-

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ichiometry using agate mortar and pestle, first in air atmosphere for 2 h and then in methanol for 1 h. The mixture was calcined at an optimized temperature/time (1050 °C/12 h). A small amount of polyvinyl alcohol (PVA) was added to the calcined powder for fabrication of pellets (as binder material). The calcined fine powder was cold pressed into cylindrical pellets of 10 mm diameter and 1–2 mm of thickness by applying uniaxial pressure of $5 \times 10^6$ N/m$^2$. The pellets were subsequently sintered at an optimized temperature/time (1080 °C/6 h). PVA was burnt out during high-temperature sintering. A preliminary structural study was carried out using an X-ray diffraction (XRD) technique with an X-ray powder diffractometer (Rigaku Miniflex, Japan) for the confirmation of formation of the compound. Cu Kα radiation ($\lambda = 1.5405$ Å) was employed in the wide range of Bragg angles ($20^\circ \leq \theta \leq 80^\circ$) at a scan speed of 3° min$^{-1}$.

The surface morphology and microstructure of a sintered pellet were studied by scanning electron microscopy (JEOL-JSM, model: 5800). A pellet sample was gold coated prior to being scanned under high-resolution field emission gun of SEM. To measure the electrical properties of the compound, air drying silver paint was applied on both the flat faces of the sample. Capacitance ($C_p$) and loss tangent ($D$) were measured as a function of frequency (1 kHz to 1 MHz) at different temperatures (30–500 °C) using a computer-controlled LCR meter (HIOKI 3532 LCR Hi Tester, Japan) in conjunction with a laboratory-made sample holder and heating arrangement with an ac signal of 1.2 V. All the measurements were carried out within a small (±2 °C) temperature interval. The effect of moisture on the above properties was overcome by pre-heating of the sample to 150 °C with annealing time 2 h, and then cooled to room temperature prior to the measurements.

## 3. Results and discussion

The formation of the desired compound ($Ba_{0.9}Sr_{0.1}TiO_3$) was checked by preliminary X-ray structural analysis. Fig. 1 shows the X-ray diffraction pattern of the calcined powder of BST recorded at room temperature. The sharp and single reflection peaks of the XRD pattern, which was different (in position) from those of ingredient precursors, confirmed the formation of single-phase compound. All the peaks were indexed in different crystal systems. The lattice parameters were obtained using a standard computer program 'PowdMult' [16]. The best agreement between observed (obs) and calculated (cal) interplanar spacing ($\Sigma(d_{obs} - d_{cal}) = \text{minimum}$) was observed in the tetragonal crystal system. The least-squares refined lattice parameters of BST are: $a = 3.9571(55)$ Å, $b = 3.8651(55)$ Å (with estimated standard deviation in parenthesis).

Fig. 2 shows the scanning electron micrograph of the sintered pellet of the material at room temperature describing their surface property and microstructure. The grains are uniformly distributed through out the surface of the sample showing its compactness (high density) and homogeneity. Also, the nature and distribution of grains in the sample suggest the formation of the single-phase compound. Most of the grains are numbers of spherical shape.

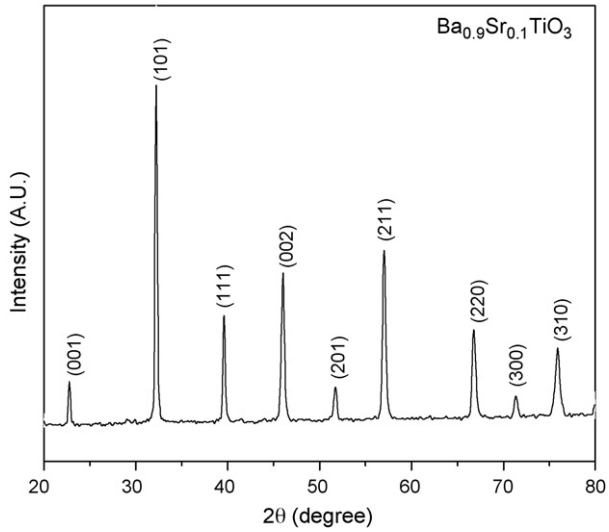


**Fig. 1.** Room temperature XRD pattern of the calcined powder of BST.

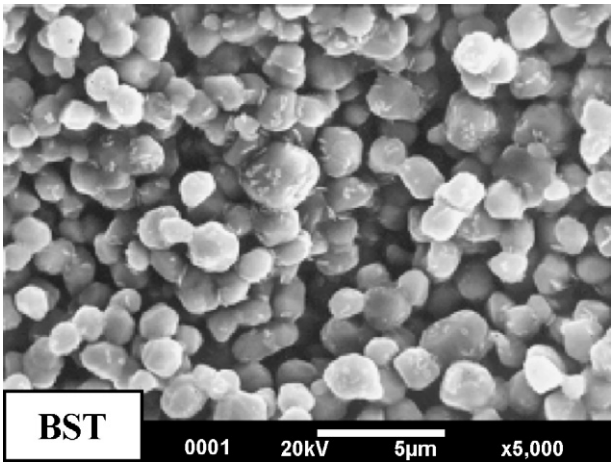


**Fig. 2.** SEM micrograph of the sintered pellet at room temperature.

Fig. 3 shows the variation of relative dielectric constant ($\varepsilon_r$) as a function of frequency at 225, 300 and 500 °C. The nature of the graphs indicates a dispersive behavior of the material at low frequencies reflecting blocking effects. Dispersive behavior of the dielectric constant is mainly due to two reasons: (i) polarized structure of studied material and (ii) associated mobile charge carriers [17]. The high value of $\varepsilon_r$ at low frequency of all the temperatures is due to presence of different types of polarizations (viz. electronic, dipolar, interfacial, ionic orientation, etc.). Further, $\varepsilon_r$ decreases with increasing frequency. This is a typical characteristic of dielectric materials [18,19].

Fig. 3(inset) shows the variation of tangent loss ($\tan\delta$) as a function of the frequency at three different temperatures. Here the value of $\tan\delta$ deceases gradually with increasing frequency up to 250 °C (not shown). The $\tan\delta$ peaks were observed at higher temperatures (≥300 °C) which shift towards the higher frequency region (with rise in temperature). This type of feature suggests the presence of dielectric relaxation in the compound [20,21].

Fig. 4 shows the temperature-dependent relative dielectric constant ($\varepsilon_r$) and loss tangent ($\tan\delta$) at 108 kHz. Initially, both the value of $\varepsilon_r$ and $\tan\delta$ increases, attains their maximum values ($(\varepsilon_r)_{max}$ and $\tan\delta_{max}$), and thereafter decreases with rise in temperature in the said frequency range. A dielectric anomaly was observed at 101 °C with $(\varepsilon_r)_{max} = 1977$ at 108 kHz. This anomaly suggests that there is

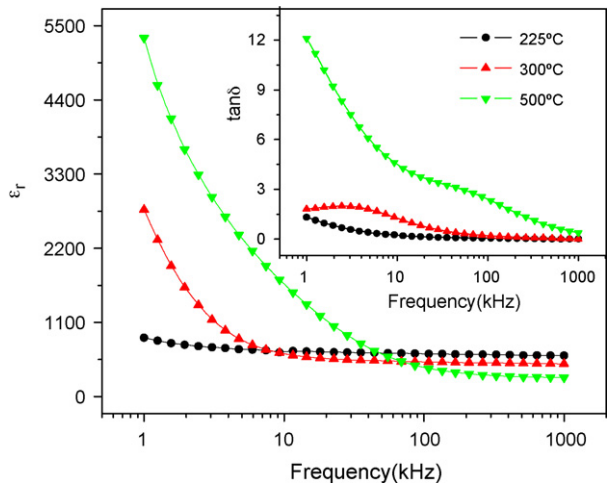


**Fig. 3.** Variation of (a) $\varepsilon_r$ and (b) $\tan\delta$ (inset) as a function of frequency at 225, 300 and 500 °C.