

Structural and dielectric properties of pure and cerium doped barium titanate

Sabina Yasmin^a, Shamima Choudhury^a, M. A. Hakim^b, A. H. Bhuiyan^c and M. J. Rahman^{c,*}

^aDepartment of Physics, University of Dhaka, Dhaka-1000, Bangladesh

^bMaterials Science Division, Atomic Energy Centre, Dhaka-1000, Bangladesh

^cDepartment of Physics, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

Barium titanate (BaTiO₃) and cerium (Ce) doped BaTiO₃ samples were prepared by the standard solid state reaction method and were sintered at 1473 K for four hours. The structural and dielectric properties of the samples were studied. The x-ray diffraction results showed mostly the BaTiO₃ phase where the lattice parameter decreased with the addition of Ce. The temperature dependent dielectric constant showed a transition temperature, which decreased with an increase in dopant content. The dielectric constant decreased with an increase in frequency and increased as the amount of dopant was increased. The alternating current resistivity decreased in the lower frequency range (1-100 kHz) and remained constant in the higher frequency range. The direct current (dc) density-voltage characteristics of the samples showed ohmic behavior for both the pure and Ce-doped BaTiO₃. As the temperature increased the dc resistivity of the samples decreased. The activation energy increased with the Ce content.

Key words: Cerium doping, Barium titanate, x-ray diffraction, Dc resistivity, Dielectric constant.

Introduction

The discovery of ferroelectric barium titanate (BaTiO₃) opens the present era of ceramic dielectric materials. BaTiO₃ having the perovskite structure with tetragonal symmetry at room temperature, possesses a relatively large dielectric constant (ϵ') and electro optic coefficient. Now-a-days BaTiO₃ has become the basic capacitor material in semiconductor technology. BaTiO₃ ceramics have a strong piezoelectric effect. These ceramics find wide applications in devices such as microphones, ultrasonic and underwater transducers, multilayer capacitors and spark generators. BaTiO₃ is one of the ABO₃ type (A = mono or divalent, B = tri-hexavalent ions) ceramic materials which have been examined in search of ferroelectric applications [1]. Doping in ABO₃ type ceramics plays an important role in improvement of their performances [2, 3]. This exhibits semiconducting properties together with a positive temperature coefficient (PTC), for which it is used as a PTC resistor. When the temperature is lowered to ~400 K, the ionic displacement of the titanium (Ti)-ion changes the crystal structure to tetragonal from cubic BaTiO₃ and it goes to a ferroelectric state. Sen and Choudhary [4] observed for calcium (Ca) modified BaSn_{0.15}Ti_{0.85}O₃ ceramics that the transition temperature shifted below room temperature as the concentration of Ca was increased in (Ba_{1-x}Ca_x)(Sn_{0.15}Ti_{0.85})O₃ and the dc resistivity decreased with an increase in temperature and hence they exhibited semicon-

ducting behavior at the higher temperature. Among the ferroelectric materials, BaTiO₃ has received enormous attention due to its simple crystal structure, high stability and extremely high ϵ' , low leakage current and anisotropic optical behavior [5]. However, the doping mechanism in the BaTiO₃ based system is not yet clear and needs deep research. The effect of Ce doping in BaTiO₃ ceramic materials has shown promising dielectric properties such as a relatively high permittivity and high endurance. Ce can exist in two oxidation states, 4+ and 3+[1]. Hwang and Han suggested that when cerium oxide (CeO₂) was added to BaTiO₃, Ce³⁺ was incorporated into the Ba²⁺ sites instead of the Ti⁴⁺ sites[7]. In view of this, Ce doped BaTiO₃ has been synthesized by a conventional solid state reaction method. Here the structure of these ceramics has been investigated by x-ray diffraction (XRD). The electrical properties such as frequency and temperature dependent resistivity, dielectric constant (ϵ') and loss tangent ($\tan\delta$) were studied. The dc density-voltage (J-V) characteristics as a function of temperature were also investigated. The results of these observations are discussed in this paper.

Experimental Procedure

A conventional solid state reaction method was used to prepare the BaTiO₃ and doped BaTiO₃ samples. The general formula for the samples is Ba_{1-x}Ce_xTiO₃ where x = 0.0, 0.01, 0.02, 0.03 and 0.04. Appropriate amounts of BaO (BDH, England), TiO₂ (Merck, Germany) and CeO₂ (Merck, Germany) were ground and ball-milled for 24 hours in a wet medium. The homogeneous mixture was then calcined at 1173 K for 4 hours and disc-shaped samples of

*Corresponding author:
Tel : +880-2-966-5650
Fax: +880-2-861-3026
E-mail: mjarahman@phy.buet.ac.bd

height 1.26 mm and diameter 10.24 mm were formed at a pressure of 20 MPa. Finally, the samples were sintered at 1473 K for 4 h using a Carbolite 2132 furnace. The capacitance (C) and tand were measured by a Hewlett Packard Impedance Analyzer; Model 4192A. For the electrical measurements both sides of the samples were pasted with conducting silver paste (Demetron, Leipzigerstr. 10, Germany) after polishing. The x-ray diffraction (XRD) measurements were carried out using a PHILIPS X Pert PRO MPD (Netherlands) x-ray diffraction system with CuK_α radiation. The dc electrical measurements were performed at different applied voltages and at different temperatures on samples of different thicknesses. The current through the samples was recorded by a Keithley 614 Electrometer (Keithley Instruments, USA). The temperature was recorded using a chromel-alumel thermocouple placed very close to the samples.

Results and Discussion

Fig. 1 shows the XRD patterns of the samples with different Ce contents. The positions of the diffraction peaks confirmed that all the studied samples are mainly of the BaTiO_3 phase with a small secondary phase detected as BaTi_2O_5 . The diffraction peaks for the BaTi_2O_5 phase may be due to the preparation of samples using raw BaO , CeO_2 and TiO_2 . Due to Ce doping the peak intensity such as of (21 $\bar{1}$) and (022) reflections of the BaTi_2O_5 phase increases slightly, which means that the formation of BaTi_2O_5 phase is enhanced slightly with Ce doping. This increase may be due to substitution of smaller Ce^{+3} ion (radius = 0.102 nm with 6 coordination number) for larger Ba^{2+} ion (radius = 0.135 nm with 6 coordination number) [8] and/or due to the formation of grain boundaries. Dopant Ce ions with a small radius may form the core-shell-structured fine grains and thus the secondary phase BaTi_2O_5 appears because of the segregation of small ions in the grain boundary regions, which decreased the solubility of Ce ions in BaTiO_3 [9]. All the reflection peaks were indexed and the corrected

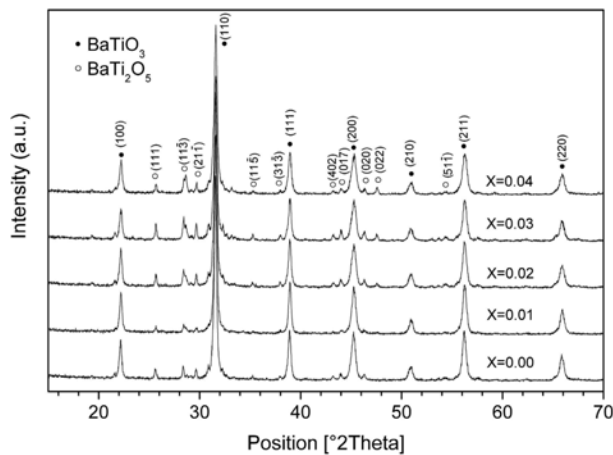


Fig. 1. XRD patterns of $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ (where $x = 0.0, 0.01, 0.02, 0.03$ and 0.04) compounds sintered at 1473 K.

Table 1. Lattice parameters, particle size (D) and transition temperatures (T_c) for different samples

$\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$	Lattice parameter (nm)	D (nm)	T_c (K)
$x = 0.00$	40.126	51.24	383
$x = 0.01$	40.101	43.24	373
$x = 0.02$	40.064	40.65	343
$x = 0.03$	40.046	40.98	313
$x = 0.04$	40.060	40.85	Below room temperature

lattice parameters were determined by the Nelson-Riley (NR) method using the NR function which is defined as:

$$f(\theta) = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \quad (1)$$

where θ is the Bragg angle [10].

In this method the value of the lattice parameter is determined by extrapolating the NR function $f(\theta)$ to zero. The values of lattice parameters obtained were found to decrease slightly with an increase of Ce doping and are given in Table 1. The decrease of lattice parameter is due to the replacement of Ba^{2+} of larger ionic radius with the dopant Ce^{3+} of smaller ionic radius [7, 11]. The particle size was calculated using the Debye-Scherrer equation [12]:

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

where 0.9 is the shape factor, λ is the x-ray wavelength 15.4178 nm, β is the line broadening at half the maximum intensity (FWHM) in radians and θ is the Bragg angle. It was found that the particle size decreased after Ce doping as shown in Table 1.

As there is a decrease in lattice parameter and the atomic mass of dopant Ce (140.12) is more than Ba (137.33), there may be an increase in density of the samples with Ce doping.

Fig. 2(a-e) show the variation of ϵ' with temperature (T) at three frequencies 10, 100 and 1000 kHz. It is seen that ϵ' increases up to a maximum value, ϵ'_{max} , and then decreases with an increase of temperature except for the composition $x = 0.04$. The temperature at which the transition occurs is termed the Curie point, T_c , where the ceramics undergo a transition from a ferroelectric to a paraelectric phase [9, 13]. The ϵ'_{max} increases with Ce doping compared to the undoped sample. It is observed from Fig. 2(a-e) that ϵ' vs T curves measured at three frequencies are superimposed and the compounds have a maximum value of ϵ'_{max} at a particular temperature for all three frequencies. Hence they do not exhibit a relaxor property. That is ϵ' is less dependent on the applied ac field which has also been reflected in the frequency dependent ϵ'' measurement at constant temperature (Fig. 3). Fig. 2(f) shows the decrease in the ferroelectric to paraelectric phase

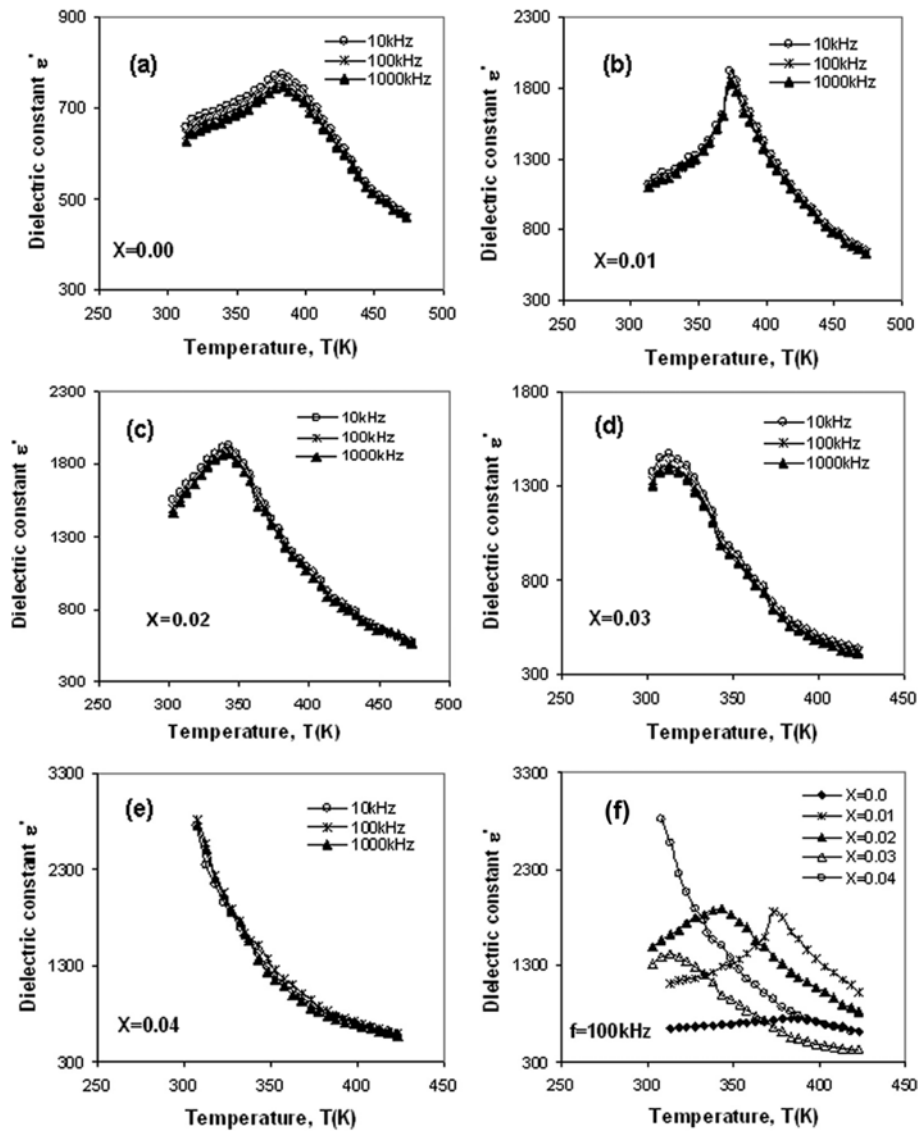


Fig. 2. The variation of the dielectric constant with temperature at three frequencies (10, 100 and 1000 kHz) of $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ compounds for (a) $x = 0.0$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$ (e) $x = 0.04$ and (f) Variation of T_c with Ce content for $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ compounds.

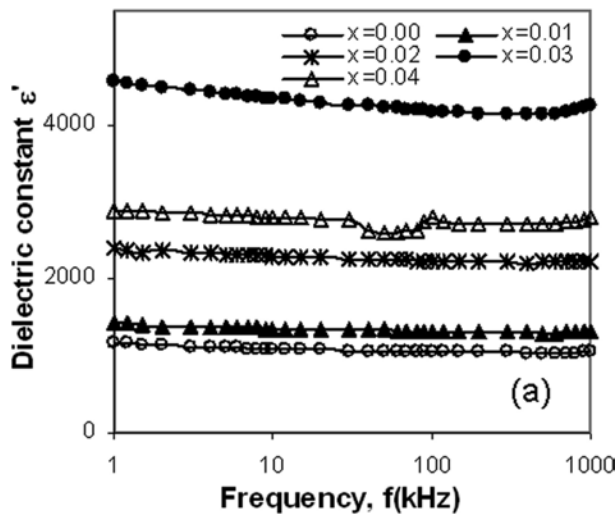


Fig. 3. Plot of dielectric constant at room temperature as a function of frequency for the samples of different Ce contents sintered at 1473 K.

transition temperature, T_c from 383 K to 313 K for $x = 0.00$ to $x = 0.03$ respectively with an increase in doping concentration. The T_c values are in good agreement with the reported data and decrease in T_c with Ce doping indicates a partial substitution of Ba^{2+} ions with Ce^{3+} into the perovskite lattice [13]. The sample where $x = 0.04$ does not manifest any sign of a phase transition implying that its T_c may be below room temperature.

Room temperature ϵ' variations of the samples with frequency up to 1000 kHz for different samples are shown in Fig. 3. The ϵ' value decreases with an increase of the frequency whereas it increases with an increase of Ce doping, except for the sample with $x = 0.03$. This type of behavior has been reported for glass doped barium titanate ceramics [14].

The $\tan\delta$ decreases with frequency for different Ce-contents as shown in Fig. 4. As the doping concentration increases the dielectric loss though becomes large in the

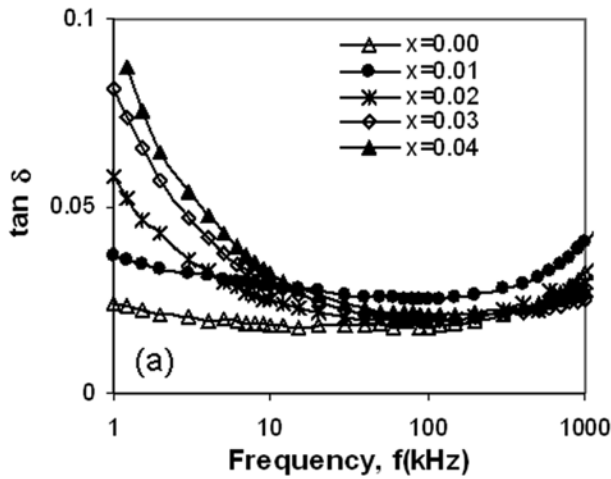


Fig. 4. Effect of Ce content on the loss tangent at room temperature for the samples sintered at 1473 K.

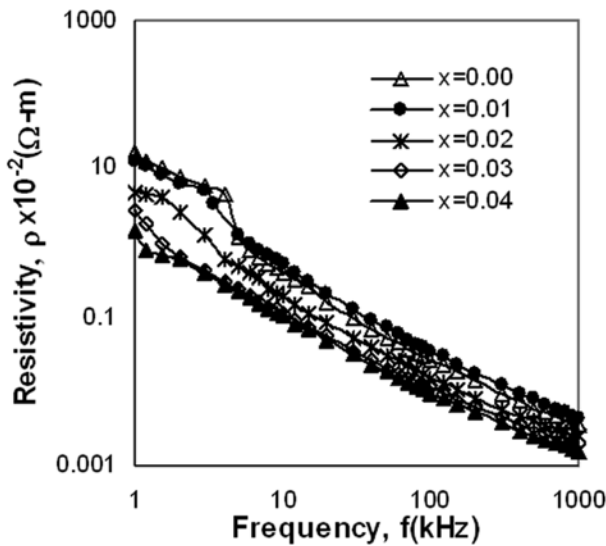


Fig. 5. The frequency dependent resistivity curves of the samples for the variation in resistivity with doping concentration.

lower frequency region but in the higher frequency region it becomes almost independent of Ce-content in BaTiO_3 with a minimum around 100 kHz.

Fig. 5 shows representative curves for the frequency dependent resistivity with different doping concentrations. It shows a decrease in resistivity with an increase in frequency and Ce content. The resistivity decrease with an increase in Ce (smaller ionic radius) doping is due to the better compaction of the samples which was also confirmed by the decrease in lattice parameter with Ce doping as shown in Table 1. Moreover, a partial substitution of Ba^{2+} ions with Ce^{3+} into the perovskite lattice also increases the carrier concentration and thus decreases the resistivity. This change in resistivity may also effect the change in T_c .

Fig. 6 shows representative J-V characteristic curves measured from room temperature to 423 K and Fig. 7 shows the variation of dc resistivity (r_{dc}) with $10^3/T$ at a

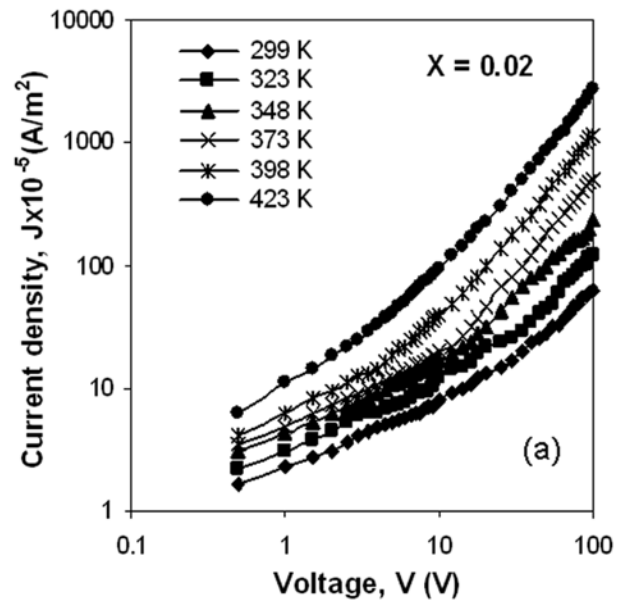


Fig. 6. Representative plots of the J-V characteristic curves.

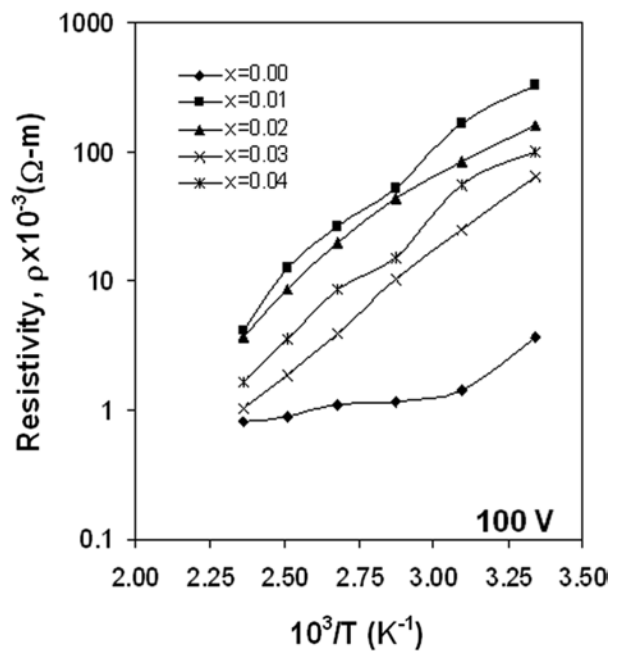


Fig. 7. Variation of resistivity of the samples with temperature at a constant voltage.

constant applied voltage of 100 V of $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ samples for $x = 0.02$. The J-V characteristics of all the samples showed approximately ohmic behavior as the n values in $J \propto V^n$ are very close to unity as shown in Table 2. The dc density (J) of the samples increases with temperature which was also found by Tannery and Cook [15] during their investigation of rare-earth doped BaTiO_3 .

The dc activation energies, E_{dc} , in the paraelectric region for all the samples have been calculated using the formula $\rho_{dc} = \rho_0 \exp(E_{dc}/k_B T)$ where k_B is the Boltzmann constant and are given in Table 2. The E_{dc} value increases from

Table 2. Values of n in $J \propto V^n$ and Activation Energy, E_{dc} of the samples for different compositions

Sample composition	n	E_{dc} (eV)
BaTiO ₃	1.1-1.3	0.07 eV
Ba _{0.99} Ce _{0.01} TiO ₃	1.1-1.6	0.38 eV
Ba _{0.98} Ce _{0.02} TiO ₃	1.3-1.7	0.39 eV
Ba _{0.97} Ce _{0.03} TiO ₃	0.9-1.3	0.38 eV
Ba _{0.96} Ce _{0.04} TiO ₃	0.9-1.1	0.45 eV

0.07 eV for BaTiO₃ to 0.38 eV for Ba_{0.99}Ce_{0.01}TiO₃. But there is no significant change in E_{dc} for further Ce additions. These values of E_{dc} suggest electronic type conduction in these materials. It is seen that the resistivity change with doping concentration is large in the lower temperature region, but as the temperature increases there is less variation in resistivity and finally it tends to saturate.

Conclusions

The XRD patterns of the samples confirmed the BaTiO₃ phase with a very small impurity phase which was enhanced slightly due to Ce doping. Owing to the replacement of Ba²⁺ of larger ionic radius with the dopant Ce³⁺ of smaller ionic radius, the lattice parameter decreased slightly with an increase of Ce content. The variation of ϵ' with temperature showed a ferroelectric to paraelectric transition and the T_c value shifted to a lower temperature having a larger ϵ'_{max} , with an increase in the amount of dopant in the ceramics compared to the undoped one. The ϵ' value decreased with an increase of frequency whereas it increased with an increase of Ce doping. As the doping concentration increases, the dielectric loss although large in the lower frequency region, it becomes almost independent of Ce-content in the higher frequency region. The dc resistivity decreased with an increase in Ce doping concentration due to the better compaction of the samples. The J-V characteristics of all the samples showed approximately

ohmic behavior and the E_{dc} value increased with Ce doping. No significant change of E_{dc} for further Ce doping was observed. These values suggest electronic type conduction in these materials.

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