Incorporation of Donar Dopant on BaTiO$_3$ (BTO) Perovskite Structure

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Abstract: The research was done to understand the influence of nano-sized donar dopant incorporation in barium titanate (BTO) structure. Core-shell structures are stated to form while dopants are added directly to BTO. Low diffusivity of ions in solid state results such core-shell structures. Pure BTO was doped with different concentration of niobium oxide (Nb$_2$O$_5$) (0.2, 0.3 and 0.4 mol %). Single stage sintering at 1250°C, 1275°C and 1300°C was initially chosen. Soaking time was varied from 0 to 2 hours. Sintered samples were taken for further characterization. Percent theoretical density (%TD) of the sintered samples was measured. Microstructure of the sintered samples was revealed by Scanning Electron Microscope (SEM). Both temperature and frequency dependent dielectric property was measured using impedance analyzer. X-ray diffraction (XRD) and Differential Thermal Analysis (DTA) was also performed. XRD confirmed the diffusion of Nb^{5+} ions into the BTO lattice. While impedance analyzer and DTA proved the shifting of Curie temperature (T$_C$) from ~120°C to ~71°C. Enhanced dielectric property was observed by the addition of Nb$_2$O$_5$.

Keywords: Percent Theoretical Density, X-Ray Diffraction, Differential Thermal Analysis, Curie Temperature, Permittivity

1. Introduction

The field of solid state electronics is expanding day by day. Consequently, research on materials having electrical properties has been gaining importance. However, designing of such materials need to be considered sensibly. Extensive efforts have been devoted to reduce not only the size but also the weight of components in electronic devices. In doing so, interest on dielectric ceramics is increasing promptly [1].

Although all materials have more or less charged particles, some materials i.e. dielectrics have restricted mobility of charge within it. Hence, dielectric is a material which is non-conducting or insulative in nature. Yet, dielectric materials can show some sort of conductivity [2].

Due to the distinctive structural characteristics, ceramics are referred to as good dielectrics. Among the dielectric materials, those having both ferroelectric and ferromagnetic property are widely known as multiferroic (MF) materials. Barium titanate (BaTiO$_3$) is a potential candidate in electronic industries which shows multiferroic characteristics. One of the ferroelectric applications of BaTiO$_3$ (BTO) includes multilayer ceramic capacitors (MLCCs). High relative dielectric constant (~1500-2000) along with low loss of BTO is beneficial for this [3]. Other applications for BTO-based materials include piezoelectric devices, electroluminescent panels, pyroelectric elements, polymer matrix composites for embedded capacitance in printed circuit boards, heaters and sensors with positive temperature coefficient of resistivity (PTCR) etc. [4-8].

The progressive advancement in microelectronic and communication system leads us to the miniaturization of ferroelectric components. Hence, achievement of high capacitance in a small volume is the prime concern. Since the discovery of the interesting dielectric properties of BTO, several works have been reported. Since addition of dopants has always been beneficial in terms of high dielectric properties, BTO has been doped with different types of acceptor or donor dopants [4-10].

At present researchers are mainly focusing on the processing, structure and properties of these materials. They are continually trying to build up an effective structure-property relationship and find out the several processing parameters affecting the structure as well as property [5].

Among the various dopants, niobium oxide (Nb_2O_5) has been widely used with both solid state and chemically synthesized BTO to manufacture high and low fire ceramic capacitors meeting EIAA, X7R and Y5V specifications [11]. In fact, it was one of the first dopants studied and has been used successfully for the last 30 to 40 years in BTO based capacitor formulations.

Nb_2O_5 is a donar dopant which has been reported as a good shifter of temperature co-efficient of capacitance (TCC) and grain growth inhibitor while doped in BTO [12-14]. However, the greatest advantage of Nb_2O_5 addition in BTO based ceramic formulations is that it is a powerful Curie temperature (T_C) shifter. This property makes Nb_2O_5 one of the most widely utilized dopants for air fired dielectric systems. It is also used as a major constituent of Y5V relaxor dielectrics based on lead zirconate titanate or $Pb(Zr,Ti)O_3$ (PZT) [15].

Hence, in this investigation, study of structure-property relationship on addition of Nb_2O_5 in BTO ceramics via solid state route was done.

2. Experimental Procedure

Conventional mixed oxide solid state synthesis route was followed preparing $BaTi_{1-x}Nb_xO_3$ ceramics where x=0.002 (0.2 mol %), 0.003 (0.3 mol %) and 0.004 (0.4 mol %) using pure $BaTiO_3$ powder [size: 60~100 nm; manufacturer: Inframat (USA); purity: 99.99%] and Nb_2O_5 powder [size: 50~150 nm; manufacturer: Inframat (USA); purity: 99.99%].

Appropriate weight of powders was mixed in a laboratory type high-density polyethylene (HDPE) pot mill. Yttria (Y_2O_3) stabilized zirconia balls manufactured by Inframat (USA) were used for milling. Two different size of balls (dia=5 mm and 3 mm) and ethanol (purity>99% Merck, Germany) as the milling media were used. Locally made motor driven ball mill having ~150 rpm was used for this purpose. Milling time was varied from 16-20 hours for each cycle.

After ball milling, the extracted wet powder was dried at 100°C-24 hours in a drier. Then the dried powder was again hand milled using mortar-pestle.

Next, the powder was pressed into pellets using HERZOG pellet press, (Model No. HTP 40, Germany) at a pressure of ~150 MPa for 2 minutes. Around 13 mm dia and 2 mm thickness of pellets were prepared. PVA (Poly vinyl alcohol) was used as binding agent during the compaction.

A chamber type muffle furnace (Nabertherm, Model No. HT 16/18, Germany) was used to sinter the pellets in ambient atmosphere. Samples were heated at 500°C-1 hour to remove binder followed by sintering at varying temperature (1250-1300°C) and soaking time (0-2 hours) with controlled heating and cooling rate (3°C/min).

Finally, sintered samples were taken for the measurement of percent theoretical density (%TD) and grain size. The microstructure of the sintered samples was examined using Scanning Electron Microscope (ZEISS EVO-18, Germany). X-ray diffraction (XRD) patterns were analyzed by Bruker D8 Advance diffractometer (40 kV, 40 mA) with Cu K_α having wavelength λ=1.5418 Å. DTA was done to evaluate the phase

transition temperature. Further, temperature and frequency dependent dielectric properties were measured using precision impedance analyzer (Model No. Wayne Kerr 6500 B series).

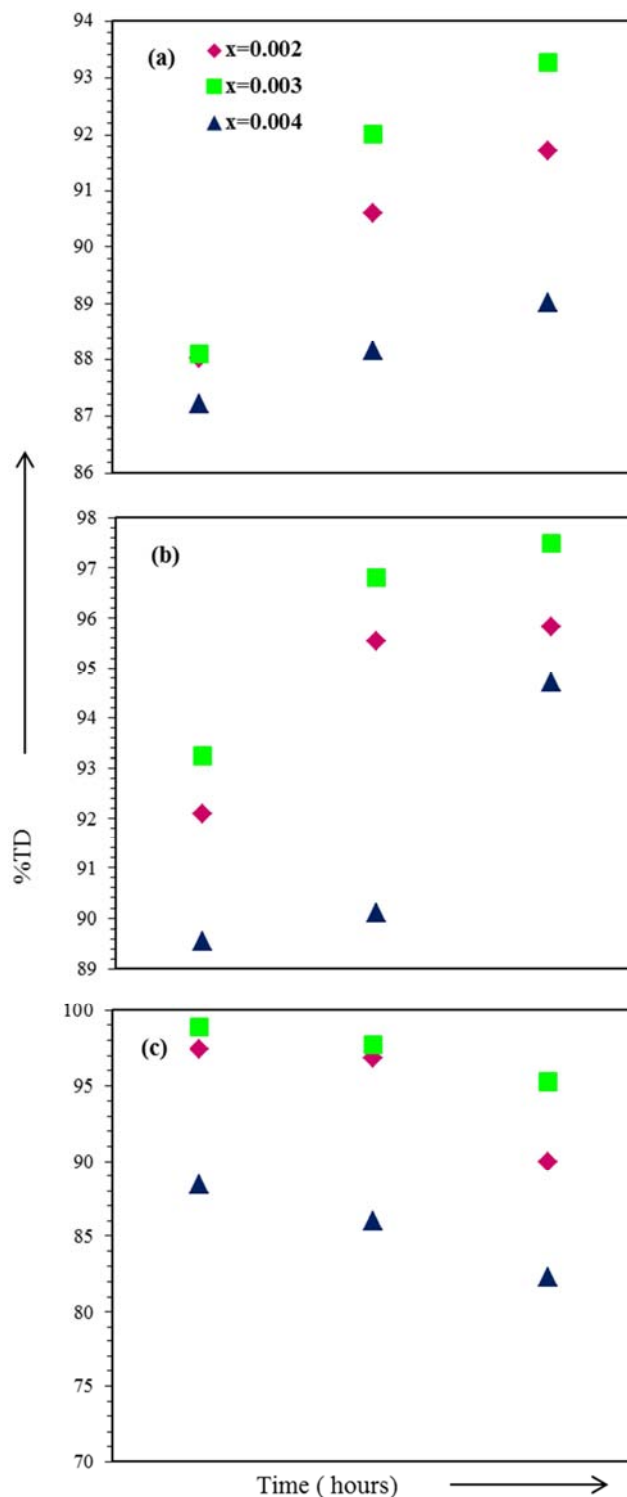## 3. Results and Discussion

3.1. Density Measurement

Figure 1. Variation of %TD with soaking time for samples sintered at (a) 1250°C, (b) 1275°C and (c) 1300°C.

Fig. 1 (a-c) shows the variation of percent theoretical density (%TD) with increasing sintering temperature as well as soaking time for single stage sintered samples. Experimental density was measured using Archimedes principle. Percent theoretical density was calculated using (1):

$$\%TD = \frac{\rho_{actual}}{\rho_{theoretical}} \times 100\% \qquad (1)$$

Highest density was achieved for the composition of x=0.003 or $BaTi_{0.997}Nb_{0.003}O_3$ ceramics sintered at 1275°C for 2 hours. Selection of 1300°C as sintering temperature didn't provide satisfactory result. Sintering at high temperature along with longer soaking period might cause excessive grain growth.

On the other hand, for the samples with x=0.004, obtained density was always pretty low. The phenomenon can be explained by the fact of solid solubility limit. It is assumed that the solubility limit of Nb_2O_5 in BTO was only 0.3 mol % in this case. Formation of second phases due to the substitution of Nb^{5+} to Ti^{4+} sites and hence the segregation of Ti^{4+} out of BTO grains for x=0.004 might have an adverse effect on densification. Similar occurrence has been reported previously [16-18]. Presence of secondary phases was also evidenced in XRD and SEM micrographs shown later in this paper (Fig. 2 and Fig. 6).
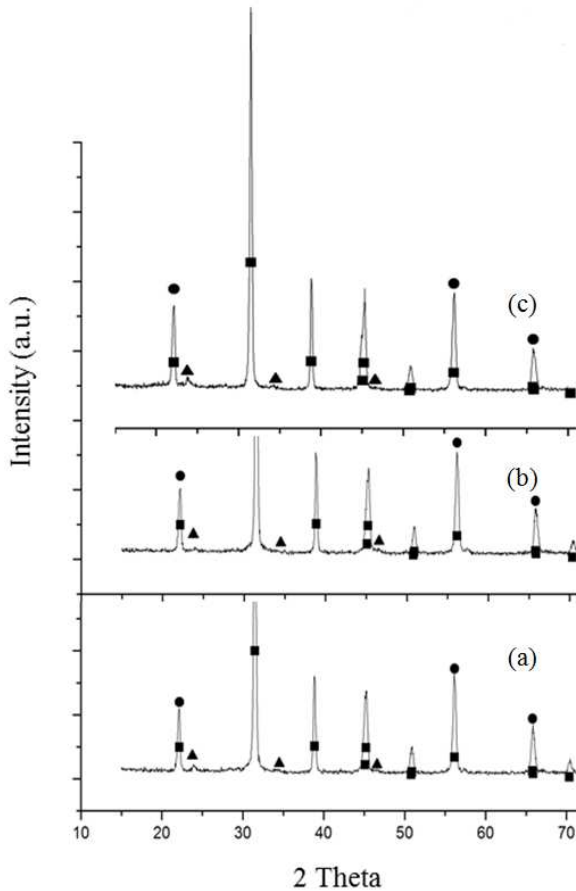
3.2. X-ray Diffraction (XRD)

The XRD patterns were further evaluated for phase identification. Fig. 2 (a-c) confirms the formation of perovskite phase (shown with symbol ■) with some secondary phases (shown with symbol ▲ and ●). However, further investigations are required to identify the second phases, which was beyond the scope of this work.

The existence of twin peaks corresponding to the 2θ value of 45° indicates the presence of single phase perovskite structure. However, with increasing the dopant concentration, slight shifting of peaks at lower angle was visible which validates the incorporation of Nb^{5+} ions in BTO lattice. The patterns also reveal the existence of large amount of secondary phases for x=0.004. Nevertheless, generation of second phases could not be avoided for other compositions due to the high temperature vacancy creation.

3.3. Differential Temperature Analysis (DTA)

The DTA curves presented in Fig. 3 (a-c) illustrate the shifting of Curie peak for Nb_2O_5 doped BTO samples. It turns out that, incorporation of Nb^{5+} ions displaced the T_C value from ~120°C (for pure BTO) to some lower temperature. With increasing the concentration of Nb_2O_5, Curie peak shifted from 72.7°C (x=0.002) to 67.7°C (x=0.004) in this investigation. This statement is also supported by previous works for different perovskite structures [18-22].

As it is well-known that, Curie temperature is influenced by various factors like composition, grain size, oxygen vacancy concentration, internal stress, particle size etc. [18], pinning effect of Nb^{5+} might have a remarkable effect on T_C shifting.
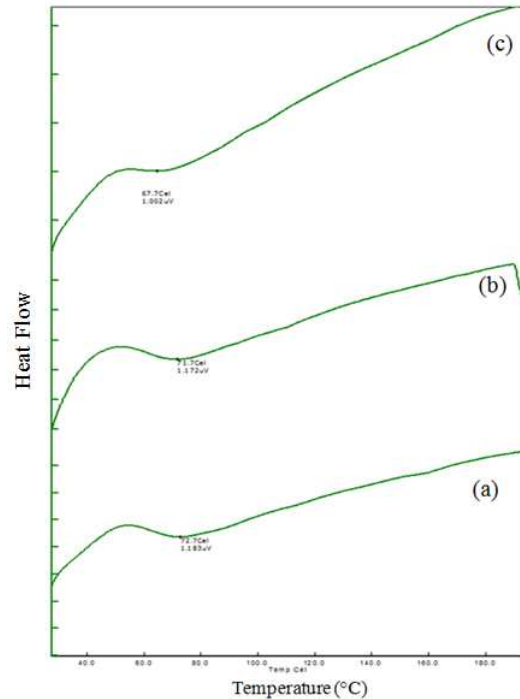

Figure 2. *XRD patterns of BaTi₁₋ₓNbₓO₃ ceramics where (a) x=0.002, (b) x=0.003 and (c) x=0.004.*

Figure 3. *DTA curves for Nb⁵⁺ doped BTO where (a) x=0.002, (b) x=0.003 and (c) x=0.004.*
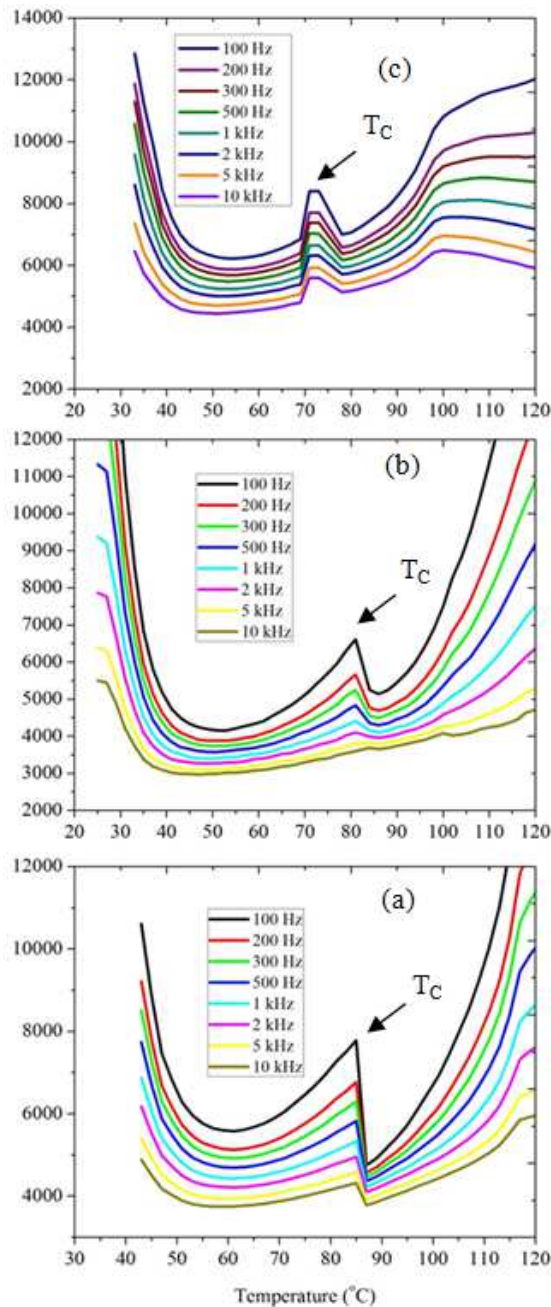
3.4. Curie Temperature Determination

Figure 4. *Permittivity curves for doped BTO samples at varying frequency & temperature with (a) x=0.002, (b) x=0.003 and (c) x=0.004.*

Fig. 4 (a-c) shows temperature and frequency dependence dielectric property for the doped samples. The shifting of Curie temperature to lower temperature is also visible in this case. Hence, it justifies the results obtained from DTA curves. However, as the concentration of Nb_2O_5 increased the peak became more and more broaden. The progressive augmentation phenomenon can be explained by the fact of compositional segregation. Compositional inhomogeneity attributed to the incidence of core-shell structure formation. In the samples with low doping level, the core-shell structure was inconspicuous. However, with increasing dopant

concentration, the degree of inhomogeneity was more severe, causing obvious core-shell structure which resulted diffuse peak. These results are analogous with former reports [18-24]. However, it is to be noted that, reduction of oxygen vacancies was expected with the increment of dopant level, which might be one of the prime factors of enhanced dielectric properties of the doped samples in this case.
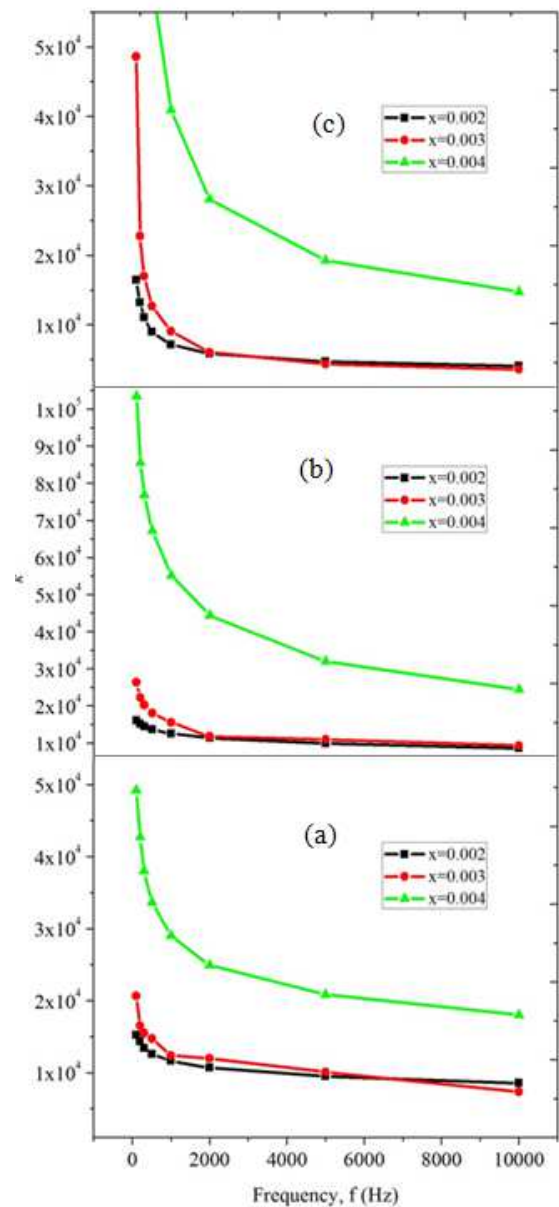
3.5. Dielectric Property Measurement

Figure 5. *Permittivity (k) vs frequency (f) curves for (a) x=0.002, (b) x=0.003 and (c) x=0.004.*

Permittivity vs frequency curves for Nb_2O_5 doped BTO samples are represented in Fig. 5(a-c). Chronological increment in dielectric constant *(k)* with increasing the amount of niobium oxide was observed for the doped samples. $BaTi_{0.996}Nb_{0.004}O_3$ ceramics gave highest *k* value. This can be enlightened by the theory of diffusion mechanism. Enhanced

concentration of Nb^{5+} ions increased the possibility of substitution of Ti^{4+}, which in turns increased the degree of polarization. As a result the dielectric property enhanced for all x=0.004 samples. The dielectric constant was calculated using (2):

$$k = \frac{Cd}{\varepsilon_o A} \qquad (2)$$

Substitution of Nb^{5+} ions by Ti^{4+} basically compensated oxygen vacancies which in turn modified the dielectric property for Nb_2O_5 doped BTO ceramics.

3.6. SEM Micrographs

The microstructure of sintered samples was observed under SEM (Fig. 6). It reveals the significant effect of sintering temperature on microstructure. Increment in grain size with sintering temperature as well as soaking time was clearly evident in SEM micrographs. However, sintering at 1300°C caused excessive grain growth. This statement is also supported by density reports.
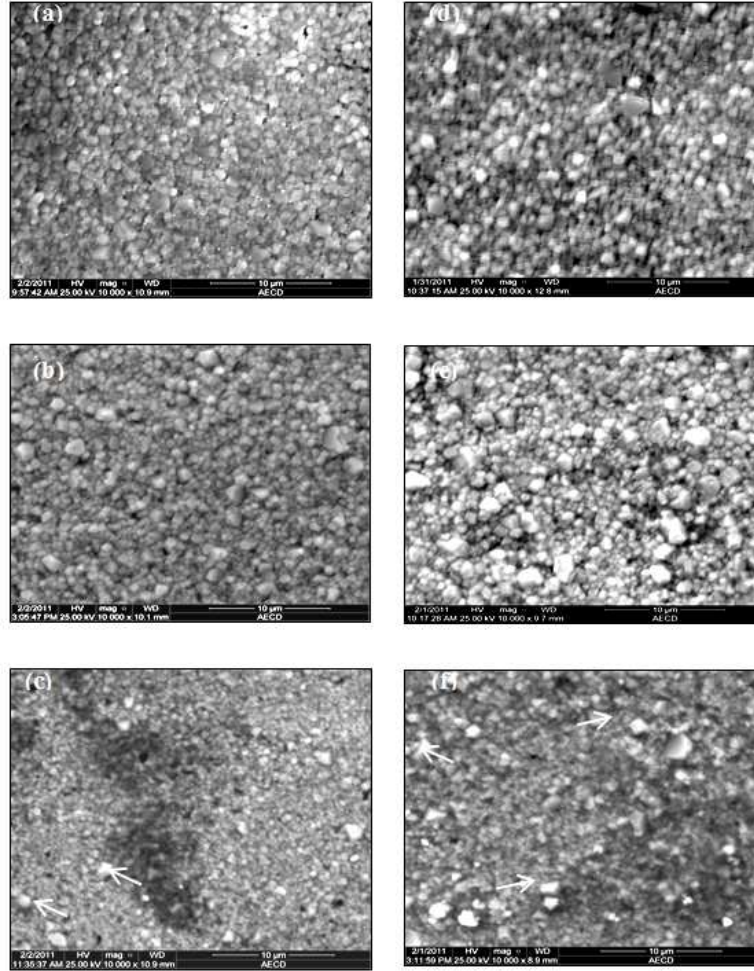

Figure 6. *SEM micrographs for samples sintered at 1275°C-2hours where (a) x=0.002, (b) x=0.003 and (c) x=0.004 and 1300°C-2hours (d) x=0.002, (e) x=0.003 and (f) x=0.004.*

On the other hand, in terms of Nb^{5+} concentration in solid solution, $BaTi_{0.998}Nb_{0.002}O_3$ and $BaTi_{0.997}Nb_{0.007}O_3$ always gave better %TD than $BaTi_{0.996}Nb_{0.004}O_3$ samples. This can be elucidated by the theory of grain growth inhabitation by pinning effect. It is believed that, there is a threshold value of Nb_2O_5 in BTO, which was 0.3 mol % in this case. Below this value there was negligible pinning effect, while above this threshold value (0.4 mol % Nb_2O_5) excessive pinning might have caused adverse effect on structure. Grains of secondary phases are also visible for 0.4 mol % samples (shown with arrow marks).

4. Conclusions

Addition of donar dopants like niobium oxide had significant effect on microstructure. It gave excellent pinning which controlled the excessive grain growth at high temperature. SEM showed that, with increasing the concentration of dopants, the pinning effect increased and thus the grain size decreased steadily. But some exception was present. XRD patterns revealed the diffusion of Nb^{5+} ions in BTO crystal structure. Dielectric constant also increased by the addition of dopant. The ferroelectric to paraelectric

transition peak depressed and k value became constant at higher frequency. Curie temperature shifted to lower temperature. This result was confirmed from the temperature dependent dielectric constant and DTA curves. Although addition of dopant above 0.3 mol % generated large number of second phase, still it improved the electrical property of BTO-based ceramics. Hence, incorporation of Nb_2O_5 donar dopant in BTO lattice is a good scope of research. Further investigations are required to understand its effect on other properties i.e. mechanical, optical etc.

Nomenclature

Symbol	Meaning	Unit
ρ_{actual}	Actual density	gm/cc
$\rho_{theoretical}$	Theoretical density	gm/cc
C	Capacitance	F
d	Distance between plate	mm
A	Area of the plate	mm^2
ε_o	Permittivity of vacuum	F/mm
k	Dielectric constant	-

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