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Original Research

Characterization and Phase Transitions of Bi Doped $BaTiO_3$ Ceramics Prepared through Chemical Route

Sreenu K[1]*, Bhargavi T[2] and Kebede Legesse Kabeta[1]

[1]Department of Physics, College of Natural and Computational Sciences, Wollega University,
Post Box No: 395, Nekemte, Ethiopia

[2]Department of Computer Science and Engineering, Sri Indu College of Engineering and Technology,
Ibrahim Patnam, Rangareddy Dist -501510, Andhra Pradesh, India

Abstract

Nano particulate Barium Bismuth Titanate ($BaBi_xTi_{1-x}O_{3-\delta}$) materials (with x=0.05, 0.1 and 0.15) were prepared through sol-gel chemical route (Pichini method) and the XRD patterns were indexed on the basis of tetragonal-$BaTiO_3$ phase. In higher Bi-content secondary peak was observed. In the study of lattice parameters, C-parameter is found to be decrease with Bi-content. With increasing in the Bi-content the percentage of secondary absorption peak is increases. The microstructure of the samples was investigated by using Scanning electron microscope (DSC). The grain size range was 80 nm for the dried gel powder and 1-1.5 μm for the powder calcined at ≈ 1150°C. Infrared (IR) spectrum was recorded at room temperature with Thermo Nicolet Nexus 670 FTIR spectrometer. The secondary absorption peak observed at 435 cm^{-1} was found to decrease with Bi-content. In the study of lattice parameters, C-parameter was found to be decrease with Bi-content.

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***Corresponding Author:**
Sreenu K
E-mail:
cnukasam@gmail.com

INTRODUCTION

The origin of ferroelectricity in BT-based compounds is attributed to the crystalline-nature of the perovskite and possessing large internal-electric field. The ferroelectric order in the materials mainly depends on distortion of oxygen octahedra. It has been reported in the literature that ferroelectric properties of the Aurivillius family of bismuth oxide-layered compounds is mainly due to the Bi^{+3} lone pairs and these layered materials have perovskite structure with the ABO_3 formula, where cation A-site contains stereo-active lone pair electrons of Bi^{+3}. The interesting and striking feature of the electronic-polarization and ferroelectricity observed in the layered-bismuth compounds is mainly due to the bismuth oxide lone pair electrons (Prasad *et al*., 2009, Yet-Ming Chiang *et al.,* 1998).

The electrical properties of $BaTiO_3$-based ceramics were found to be sensitive to microstructure as well as defect-chemistry of the materials (Syed Mahaboob *et al.,* 2005 and 2006). The defects are once again strongly influenced by chemical-composition, sintering conditions and method of preparation (solid state, solution, hydrothermal, microwave etc). The preparation of $BaTiO_3$ by conventional solid state method involves high-sintering temperature (greater than 1200°C) and therefore to reduce sintering-temperatures, sol-gel route is generally adopted. Sol-gel route not only lowers materials sintering temperature but also gives homogeneous final product (Jitianu *et al.,* 2003, Nowotny *et al.,* 1991 and Chan *et al.,* 1976).

The perovskite $BaBiO_3$ is a well known semiconductor (Vineis *et al*., 1996), and exhibits superconductivity when bismuth ion is substituted by K^+ ion (Sleight *et al.,* 1975 and Matthes *et al*., 1988). The charge neutrality in this perovskite demands equal (1:1) ratio for Bi^{3+} (with $6s^2$) and Bi^{5+} (with $6s^0$) and therefore the chemical formula can be written as $Ba^{2+}Bi_{0.5}{}^{3+}Bi_{0.5}{}^{5+}O_3$. It crystallizes in monoclinic lattice, with Centro symmetric I2/m space group. The electrical conductivity behavior of $BaBiO_3$ was attributed to charge dispersion phenomena (Ying Luo *et al.,* 2006).

It is also reported that the partial substitution of Bi^{+3} by trivalent cation at A-site or pentavalent cation at B-site, causes a transformation from insulating behavior to semi-conducting behavior. In view of this we have chosen $BaBiO_3$ at one end and $BaTiO_3$ on the other end. A systemic study of these properties of $BaBi_xTi_{1-x}O_{3-\delta}$, with an intermediate novel composition between the mentioned above two ends, will be worth investigating, for further understanding of unusual electrical behavior. Moreover, the coordination, the bonding with different oxidation states of A- and B-sites, the rotation of BiO_6 octahedra, (Sreenu *et al.,* 2010 and 2011) competitive distortion and tilting can easily be elucidated. In the present investigation, we reported the detailed studies of the novel $BaBi_xTi_{1-x}O_{3-\delta}$ [x = 0.05 (BBT1), 0.1 (BBT2) and 0.15 (BBT3)] ceramics.

MATERIALS AND METHODS

Notation of samples nominative and sintering protocol is given in table1. The sol–gel method widely used to produce nano crystalline $BaTiO_3$ powders and films. This process involved dissolving the metal-containing compounds in the solvent, hydrolyzing to polymeric condensation, drying the resulting solution into various gels, and, finally, annealing the gels at high temperature to form $BaTiO_3$ nano crystals (Frey *et al.,* 1993 and 1996). In this process, the choice of starting materials, concentration, pH value, and heat treatment schedule had a strong influence on the properties of the $BaTiO_3$ nanoparticles. However, the different rates in the hydrolysis and condensation of Ba and Ti precursors often led to chemical component segregation in the obtained gels. To avoid this problem, acetic acid was used to modify the hydrolysis rate of the Ti precursor (Frey *et al.,* 1993, Zhang *et al*., 2000 and Thomas *et al.,* 2001). It has been reported in the literature that, the pH value of the solvent of BT based materials has great influence on colloid formation, gel structure, grain size distribution, and degree of aggregation (Luan *et al*., 2001, Liu *et al.,* 2001 and Raghavender, 2013). If pH value is below 7, no gel is formed and the obtained powder has a strong degree of aggregation. However, increasing the pH value to 8, the nanoparticles obtained at 600^0C. The stachometric amounts of barium nitrate $(Ba(NO_3))_2$ (Merck 99%) and bismuth nitrate $(Bi(NO_3)_3 5H_2O)$ (Merck 99%) are taken in aqueous solution and titanium dioxide(TiO_2) dissolved in HF solution (Titanium peraxocomplex) is added to the solution. It may be noted here that the Bi is an element with multiple valency of +3 and +5 and is assumed to substitute for Ti^{+4} in B-site. The mixture is slowly heated on a hot plate and citric acid is added. The pH value is adjusted to desired value by adding ammonium hydroxide solution. Ethylene glycol is added to the mixture and heated till precursor is obtained. The precursor is burned at 600^oC for 5 hours. Finally the resultant powder was crushed and pressed into circular pellets of 10 mm diameter and ~ 1mm thickness. The detail synthesis protocol (Sreenu *et al*., 2011) the possible chemical reactions are as follows:

$$Ba(NO_3)_2 + TiO_2 \rightarrow BaTiO_3 + 2NO_2 + 1/2O_2$$

$$Ba(NO_3)_2 + Bi(NO_3)\ 5H_2O \rightarrow BaBiO_3 + 3NO_2 + 5H_2O$$

$$Ba(NO_3)_2 + x\ Bi(NO_3)\ 5H_2O + (1\text{-}X)\ TiO_2 \rightarrow BaBi_xTi_{1\text{-}x}O_{3\text{-}\delta} + xNO_2 + xH_2O$$

Table1: Compositions and sintering protocol.

Compound	Nomenclature	Pre-sintering Temperature	Final sintering Temperat-ure
$BaTiO_3$	BT	600^0C	1250^0C
$BaBi_{0.05}Ti_{0.95}O_3$	BBT – 1	600^0C	1175^0C
$BaBi_{0.1}Ti_{0.9}O_3$	BBT – 2	600^0C	1150^0C
$BaBi_{0.15}Ti_{0.85}O_3$	BBT – 3	600^0C	1130^0C
$BaBiO_3$	BB	600^0C	800^0C

The crystalline structure of the prepared samples was analyzed with X-ray diffraction (model Siemens D-5000) using Cu K*α* radiation with uniform scan rate (~2◦/min). The microstructure of the samples was investigated by using DSC (Hitachi N3400, Japan). The FTIR patterns were acquired by using Bruker Optics, Germany Model Tensor 27 FTIR spectrometer from 4000 cm^{-1}- 400cm^{-1}, using KBr pellet as a reference method.

RESULTS AND DISCUSSION

Structural Studies

Structural studies were carried out by X-ray diffraction with Cu-Ka radiation at room temperature. Scanning rate was 2^o/min, over a wide 2θ range of 20^o to 80^o. Figure 1 (a-e) shows room temperature X-ray diffraction (XRD) patterns obtained for $BaBi_xTi_{1\text{-}x}O_3$ ceramics. The $BaTiO_3$ and BBT1 samples show single phase formation. Analysis of the peaks (0 0 2) (2 0 0) (tetragonal), in the 2θ range 44- 46 degree is important and shown in figure 1. The splitting of (0 0 2) and (2 0 0) peaks clearly indicate the presence of tetragonal phase. The present system shows the tetragonality in $BaTiO_3$, due to the different composition mechanism, or site substitution. $BaBiO_3$ is a material with disordered perovskite structure and the present chosen composition is the combination of both phases of $BaTiO_3$ and $BaBiO_3$ which seems to become into a composite for higher Bi content (Sreenu. K *et.al* (2011)). In BBT2 sample the secondary phase peak (i.e.$BaBiO_3$) appeared at 28^0 of 2θ angle and the peak percentage is 11%, compared to the 100% peak of the $BaTiO_3$ Fig [1 c] .From the XRD patterns, it is observed that with increasing Bi content this peak percentage is also increasing. The (101) peak at higher Bi concentrations (x=0.1 – 0.15 of Bi) shifted towards lower angle side, and such shifts may be attributed to the fact that Bi enters into Ba site up to 0.01, and later goes to the Ti site. The excess amount Bi is formed as a secondary phase i.e. $BaBiO_3$ and it implies that Bi^{3+} ions replaces Ba^{+2}, since the ionic radii of Bi is small (1.17 Å) as compared to Ba (1.61 Å). All XRD peaks for doped $BaTiO_3$ were indexed on the basis of tetragonal structure and lattice parameters were calculated using POWD software by least square refinement method. The values of lattice parameters for $BaTiO_3$ system are found to be a=b= 3.9982 (A^0) and c= 4.021(A^o). (ICDD file no 15-453). The c- parameters is found to decrease with Bi-content, the small variation is observed up to the sample BBT2 and on BBT3 onwards the c-values are varying drastically because of the secondary phase influencing the lattice parameter values, the peak percentage is increasing the lattice parameters and the volume also are decreasing.

Micro Structural Properties [SEM] of $BaBi_xTi_{1\text{-}x}O_3$ ceramics

The microstructure of the samples of the all the BBT compositions is shown in figure 2 (a-d) and the average grain size measured by linear intercept method and also included in Table 2. It can be clearly seen from the micrographs that the Bi ion substitution has a strong effect on the grain size in other words the grain size of the sample increases with increase in bismuth content, and the average grain size of BBT1 is 100 nm. From the careful observation of the SEM photographs, it is presumed that bismuth ion is accumulated as $BaBiO_3$ at the grain boundaries, as the bismuth oxide is more volatile and has melting point far below the sintering temperature. It is observed that bismuth incorporation into BT has improved the grain growth. Grain size plays an important role in explaining different electrical properties of materials e.g. as the grain becomes finer (~1.5 μm) the strain decreases and hysteresis becomes smaller as reported for $BaTiO_3$ (Uchino *et al.,* 1989) reported that tetragonality

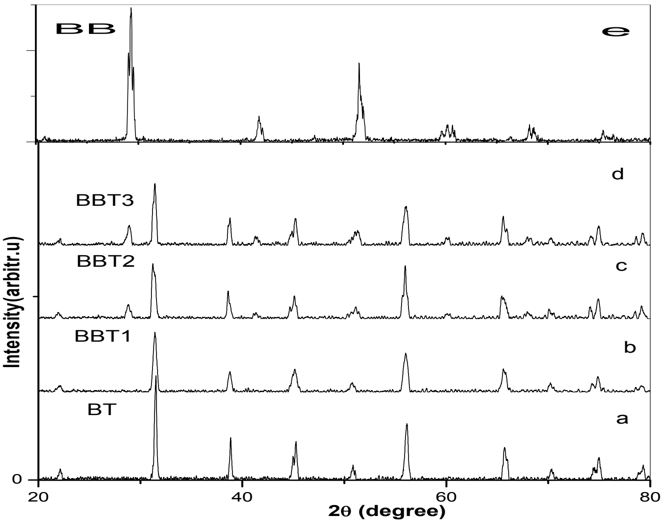

Figure 1: XRD patterns of BBT ceramics.

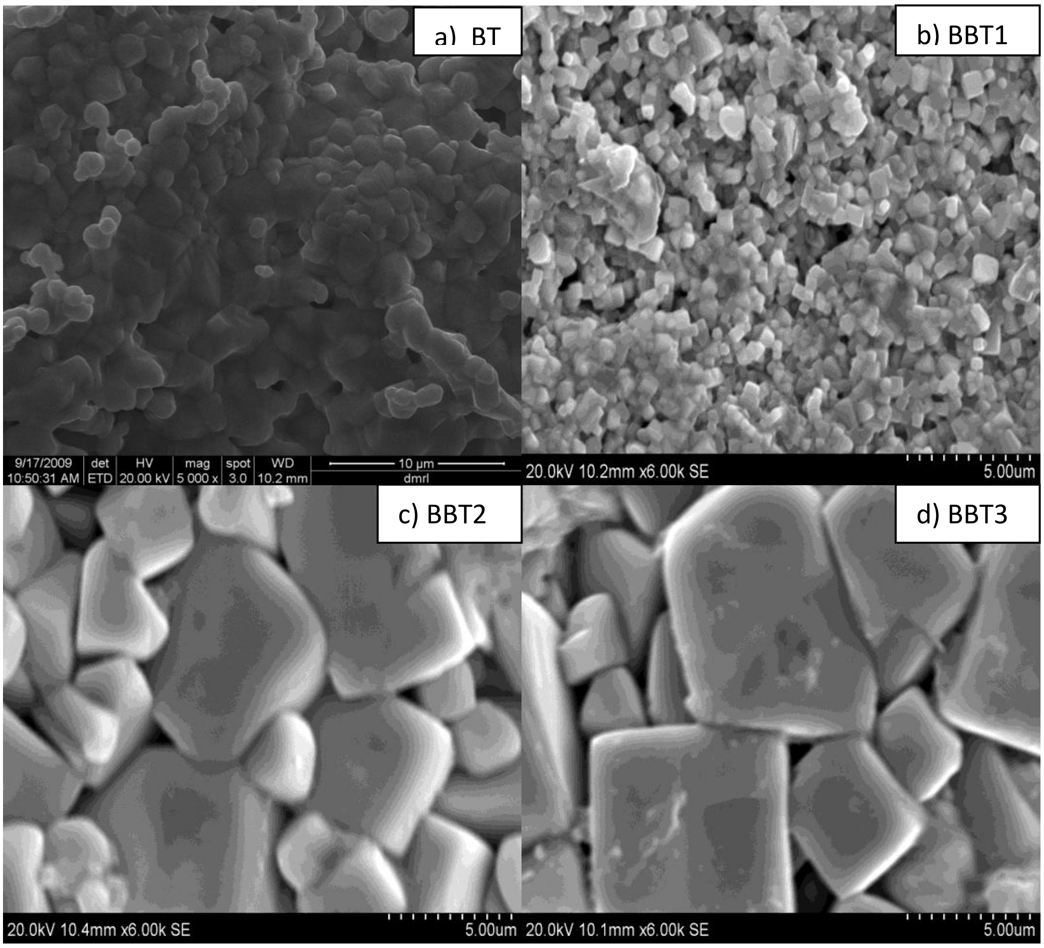

Figure 2: SEM pattern of BBT ceramics.

Table 2: Lattice parameters and crystallite size of BBT ceramics.

Sample Name	a Å	c Å	b Å	Percentage of Density gm/ cm^3	Volume cm^3	Crystallite size (XRD) nm	Grain size (SEM) μm
BT	4.03 3.99*	4.00 4.03*		88	65 64.36*	90	90 nm
BBT1	4.00	4.02		91	64	75	1.75
BBT2	4.04	2.86		92	58	74	2.65
BBT3	4.00	2.84		93	53	75	3.44
BB	6.33 6.19*	8.62 8.67*	6.12 6.17*	94	320 328*	85	-

* Reported

decreases drastically below grain size of ~0.2 µm and the system becomes cubic with c/a = 1. It is presumed from the SEM photographs that bismuth ion is accumulated as $BaBiO_3$ at the grain boundaries, as the bismuth oxide is more volatile and has melting point far below the sintering temperature. Finally, it is observed that bismuth incorporation into BT has improved the grain growth.

From the pictures it is clear seen that the cubic shape of the grains is observed, pores are located at grain boundaries and it is also seen that the grain size increases considerably with increasing the bismuth (Bi) content, which is attributed to the presence of bismuth oxide in liquid-phase form in grain boundary region. The melting point of bismuth oxide is about 850^{o}C and the sintering temperature of the present composition is around 1150^{o}C, which is much higher than that of melting point of bismuth oxide. It is a known fact that the driving force of the grain growth is mainly dependent on the elimination of the grain boundary area and lowering of grain boundary energy and therefore the grain growth becomes dominates in the sample, with increasing Bi content.

Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra of all the samples are recorded in the range 4000-400 cm^{-1} (Figure 3). From these spectra it is seen that pure $BaTiO_3$ shows as absorption at 540 and 435 cm^{-1} which are considered to be a characteristic feature of the sample and are attributed to Ti–O band and Ti–O bending vibrations (Last, 1957, Perry *et al*., 1957). Oxygen octahedrons in PZT and BT are very similar, even though some ions are different, the absorption peak in the vicinity of 540 cm$^{−1}$ is assigned to the vibration of O–M (M=ion at B-site) bond. A low frequency band (below 400 cm$^{−1}$) is assigned to cation- TiO_6 vibration. The observed absorption frequency band, near 540 cm$^{−1}$, is assigned to the Ti–O_I "stretching" normal vibration the former is 537cm$^{−1}$ when the latter is 547 cm$^{−1}$. It is explained by the weakness of coulomb interaction. In the region below 1000 cm$^{−1}$ a broad band that was attributed to stretching of the M- O bond appears, where M is Ti, Ba or Ca (Last, 1957). The intensity of secondary absorption peak in the present system is found to decrease with increasing Bi-content in the chemical compositional formula, some of them enter B-site in the perovskite structure, even though most of them occupy A-site, and more over the broad absorption peak like behavior is pronounced for BBT3 sample. The two sites for Bi are the first one Bi^{+5}remains same and the other site $Bi^{+3}$is occupies by Ti^{+3} site, and therefore the average bond length Bi(1)-O and Bi(2)/Ti-O may influence the IR band on account of different ionic radius of Bi^{+3},Bi^{+5},Ti^{4+},Ti^{+3} in octahedral coordination and hence it is reflected as decreasing magnitude of secondary absorption peak in the IR spectra these band positions are given in table 3. This indicates that the samples may become more diffusive with increasing the Bi-content in the lattice. As the radius of Bi^{3+} (0.96 Å) is smaller than Ti^{4+} (0.68 Å) ion, the unit cell parameter, c, is found to decrease with increasing the Bi content. On the other hand the broad secondary absorption peak is attributed to the competitive interaction of Bi^{+3} and Ti^{4+} ions. This clearly indicates that there exists a different mechanism of secondary phases or a kind of competitive interaction. To keep electric charge balance, the amount of O-vacancies in the latter is three times as large as that in the former. Therefore, Ti–O octahedrons are distorted or damaged more easily. Resulting in the distance between Ti and O becomes shorter. An ion with less electric charge replaces Ti^{4+}, the coulomb interaction between O_2^- and the cation in B-site is weakened. Then, the wave number of the corresponding absorption peak shifts to lower frequency. When the radii of additives are very small, these ions have probability to occupy B-site and induce many O-vacancies. So, the ordinary structure of TiO_6 octahedron is distorted or damaged. The wave number of absorption peak decreases.

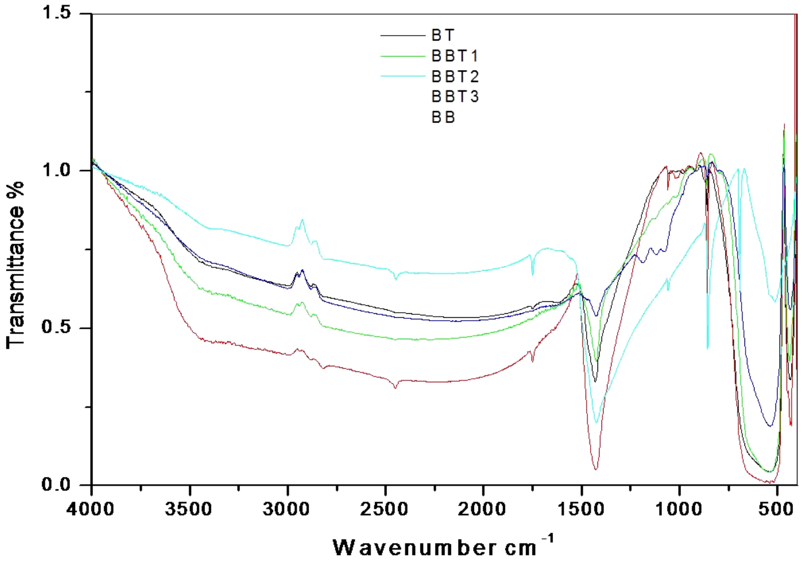

Figure 3: FTIR spectroscopy of BBT ceramics.

Table 3: Infrared band positions (cm^{-1}) of $BaBi_xTi_{1-x}O_{3-\delta}$.

Bond position	Wave numbercm^{-1}
Ba-O	1420
Ti-O	1020 895 702 540 435
Bi-O	702 520

CONCLUSIONS

In BBT ceramics, BT, BBT1 samples were showed single phase tetragonal structure and it was also confirmed by XRD analysis by showing splitting of peaks (0 0 2) and (2 0 0) of tetragonal in the 2θ range 44-46^0. In BBT2 and BBT3 by increasing the Bi-content, the percentage of secondary absorption peak increases with respect to 100% of BT peak. In the study of lattice parameters, C-parameter was found to be decreased with Bi-content. SEM results were revealed that Bi-ion substitution has strong effect on the grain size. By careful observation of SEM photographs it may be presume that Bi-ion accumulated at grain boundaries and therefore it was observed grain size increased with Bi-content. From the detailed FTIR spectra analysis, it was observed that the pronounced peak at 540 cm^{-1} which is considered to be a characteristic feature of BT. The secondary absorption peak observed at 435 cm^{-1} found to decrease with Bi-content. This is due to the fact that the Bi- content is occupying both A and B sites. Therefore this intern causes the distance of Ti-O to become shorter or tilted or distorted.

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