Characterization and Phase Transitions of Bi Doped BaTiO$_3$ Ceramics Prepared through Chemical Route

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Abstract
Nano particulate Barium Bismuth Titanate (BaBi$_{(1-x)}$Ti$_x$O$_3$) 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 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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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 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$^{4+}$ (with 6$s^2$) and Bi$^{3+}$ (with 6$s^3$) and therefore the chemical formula can be written as Ba$^{2+}$Bi$_{1-x}$Bi$_x$O$_3$. It crystalizes 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 semiconducting 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$_{(1-x)}$Ti$_x$O$_3$, 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$_{(1-x)}$Ti$_x$O$_3$ [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 table 1. 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 colloidal 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°C. The stachometric amounts of barium nitrate (Ba(NO$_3$)$_2$) (Merck 99%) and bismuth nitrate (Bi(NO$_3$)$_3$.5H$_2$O) (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 assume entered into Ba site up to 0.01, and later goes to the Ti site. The excess amount Bi is formed as a secondary phase. However, increasing the pH value to 8, the nanoparticles obtained at 600°C. The stachometric amounts of barium nitrate (Ba(NO$_3$)$_2$) (Merck 99%) and bismuth nitrate (Bi(NO$_3$)$_3$.5H$_2$O) (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 assume entered into Ba site up to 0.01, and later goes to the Ti site. The excess amount Bi is formed as a secondary phase (Sreenu. K et al (2011)). In BTB2 sample the secondary phase peak (i.e.BaBiO$_3$) appeared at 28° of 20 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 (Å) and c= 4.021 (Å). (ICDD file no 15-453). The c- parameters is found to decrease with Bi-content, the small variation is observed up to the sample BTB2 and on BTB3 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 is decreasing.

Micro Structural Properties [SEM] of BaBi$_{1-x}$Ti$_x$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.

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

| Sample Name | a Å  | b Å  | Percentage of Density gm/cm³ | Volume cm³ | Crystallite size (XRD) nm | Grain size (SEM) μm |
|-------------|------|------|------------------------------|-----------|--------------------------|--------------------|
| BT          | 4.03 | 4.00 | 88                           | 65        | 64.36*                   | 90                 |
| 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 | 6.12 | 94                           | 320       | 328*                     | 85                 |
|             | 6.19*| 6.17*|                              |           |                          |                    |

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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 BaBiO₃ 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°C and the sintering temperature of the present composition is around 1150°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.

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 Bi⁴⁺ remains same and the other site Bi⁵⁺ occupies by Ti³⁺ 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 Bi⁴⁺, Bi⁵⁺, Ti⁴⁺, Ti⁵⁺ 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 Bi⁵⁺ (0.96 Å) is smaller than Ti⁴⁺ (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 Bi⁴⁺ and Ti⁴⁺ 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 Ti⁴⁺, the coulomb interaction between O²⁻ 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 TiO₆ octahedron is distorted or damaged. The wave number of absorption peak decreases.

| Bond position | Wave number cm⁻¹ |
|---------------|------------------|
| Ba-O          | 1420             |
| Ti-O          | 895, 702, 435    |
| Bi-O          | 520              |

Table 3: Infrared band positions (cm⁻¹) of BaBi₃Tio3.5.
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°. 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 interstitial causes the distance of Ti-O to become shorter or tilted or distorted.

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