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Phase Development of Barium Bismuth Titanate by Modified Solid State Route

SOUMYA MUKHERJEE*[1], MOHAMMED SHAHNAWAZ[1] and SATHI BANERJEE[3]

Department of Metallurgical Engineering, Kazi Nazrul University, Asansol, India.
Department of Electronics & Telecommunication Engineering, Heritage Institute of Technology, Kolkata, India.
Department of Metallurgical & Materials Engineering, Jadavpur University, Kolkata, India.

Abstract

Barium bismuth titanate materials are noted for ferroelectric behavior, competitor to lead based relaxor dielectrics and even for coating having wear resistance, toughness for improving surface engineering applications. In the present context, a modified solid state process aided by agate-mortar activation for milling is carried in compare to mechanochemical milling, melt-quench method to generate the complex ceramic structure. Molar ratio of $BaO:Bi_2O_3:TiO_2$ 1:2:4 ratio have been taken with fixed soaking temperature to develop the material. Activation milling period is varied for 20 hours, 25 hours and 30 hours while soaking period descends in the order 10 hours, 8 hours and 6 hours keeping fixed temperature of about 700°C. XRD confirms the presence of peaks for all cases. Crystallite size is estimated by Scherrers formula with proper planes of index corresponding to JCPDS data. FTIR confirmed the phases developed by XRD while indicating the proper M-O bond formation from analysis in the required spectral range. EDX spectra analysis given the presence of required elements present in the sample.

Article History

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Phase;
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Morphology

Introduction

The family of bismuth oxides has been discovered by Aurivillius and the properties are found to be interest for applications as temperature stable piezo ferroelectrics. Bismuth layered crystal structures have been studied in details since majority of them have normal ferroelectrics with fairly high Curie temperature. Barium bismuth titanate is an aurivillus based ceramic compound which consists of n number of perovskite like $(A_{n-1}B_nO3_{n+3})^{2-}$ unit cell sandwiched between $(Bi_2O_2)^{2+}$ layers along pseudo tetragonal c axis. A site having 12 fold coordination of perovskite is occupied by large cations like Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+} and others while B site having 6

CONTACT Soumya Mukherjee smmukherjee3@gmail.com Department of Metallurgical Engineering, Kazi Nazrul University, Asansol, India.

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fold coordinations is occupied by small cations like Fe^{3+}, Cr^{3+}, Ti^{4+}, Nb^{5+} or W^{6+}.[1,2,3] Electric properties are noted to be anisotropic with maximum value of conductivity and major component of polarization to be parallel to $(Bi_2O_2)^{2-}$ layers. Properties of these polycrystalline materials are influenced by microstructure especially by orientation of plate like grains and by length to thickness ratio of grains. It is also noted that these bismuth layered ferroelectric structures exhibit anisotropy with high value of piezoelectric constant along a, b axis but not along c-axis. In some cases crystal may be oriented in some specific direction to achieve better properties.[4,5] Barium bismuth titanate is found to be applicable for high temperature piezoelectric sensors, non-volatile ferroelectric random access memory devices. In case of Bismuth layered ferroelectric, $(Bi_2O_2)^{2+}$ acts as insulating paraelectric layer which control the conductivity while the perovskite unit cell contributes to ferroelectricity.[1,6] Material is also found to be suitable for relaxor ferroelectrics with high dielectric, piezoelectric response over wide temperature range.[5] Material is found to be synthesized by solid state process and chemical route. Several methods like polymer precursor pechini process, sol-gel, hydrothermal, co-precipitation, mechanochemical synthesis have been carried to synthesize the material.[1,2,7,8] BBIT powders can also prepared by conventional route using $BaCO_3$, TiO_2 and Bi_2O_3 as precursor but the problem of inhomogenity in stoichometric ratio persists. Moreover there will be undesirable loss at high temperature of Bi content due to volatility of Bi_2O_3. [9,10,12] In the present context, modified solid state process assisted by agate mortar mill activation is carried. The synthesized material was analyzed by XRD to determine the phases formed followed by FTIR analysis to determine bonding and vibration of M-O coordinations followed by EDX analyses on selected areas of SEM morphology.

Materials and Methods

The precursor materials required for synthesis were AR grade Barium oxide, Bismuth Oxide and Titania. Initially, precursors were taken in proper molar ratio of $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio and then milled in agate mortar for mechanochemical activations. Milling was carried for 20 hours, 25 hours and 30 hours respectively. After milling powder samples were put into tubular furnace in presence of air atmosphere for annealing. Annealing was carried at 700°C for 10 hours, 8 hours and 6 hours soaking period respectively after milling respectively the powder samples for 20 hours, 25 hours and 30 hours respectively. Phase analysis was carried by XRD (Rigaku Ultima III) with with Cu Kα radiation whose operating condition was 40 KV, 40 mA current rating with scanning rate of 1°/min and in the range 2θ = 10-80°. For FTIR spectroscopy (IR-Prestige 21, Shimadzu) the sample was prepared by adding KBr to the sample to make a pellet by hydraulic pressure under pressure of 6t/cm^2. FTIR normal scan was carried in the range of 4500cm^{-1} to 450cm^{-1} in air atmosphere without any purging of gaseous atmosphere to maintain conditioned atmosphere. One KBr pellet was also made as the reference material for carrying the scan of the powder sample. EDX analysis (Oxford Instruments) was carried to obtain chemical analysis of the sample along with morphology of particular section of powder samples after putting the powder sample on carbon tape with gold coating for better observation without any static charging effect.

Results & Discussion

Fig 1-3 represents XRD spectra of Barium Bismuth Titanate. In all cases annealing temperature is kept fixed while with increase in milling activation period soaking time at fixed annealing temperature is decreased. As per JCPDS card no PDF# 00-035-0757 all the peaks corresponds to aurivillius $BaBi_4Ti_4O_{15}$ for all samples at three corresponding conditions. None of the samples exhibit intermediate phase or presence of precursor oxides after annealing. Crystallite size is estimated using Scherrer's formula $t=0.9\lambda/\beta Cos\theta$ where λ is the wavelength, β is full width half mean and θ is the angle in degrees. Crystallite size for Fig 1 is estimated to be about 35.11nm while for Fig 2 and Fig 3 it is estimated to be about 35.08 nm and 34.73 nm respectively. Thus, it is noted for the present experimental condition with increase in milling duration and decrease in soaking period at constant annealing temperature crystallite size decreases. All XRD spectra indicate crystalline peaks with sharp intensity without any humps or deconvulation of peaks. Three major planes of orientation (101), (109) and (110) planes are noted for all cases whilst the highest intensity peak is indexed along (109) planes.

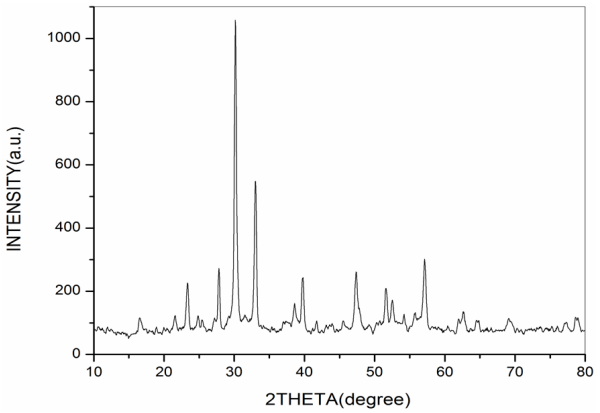

Fig 1: XRD spectra of barium bismuth titanate after milling of precursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 20 hours followed by annealing at 700°C for 10 hours

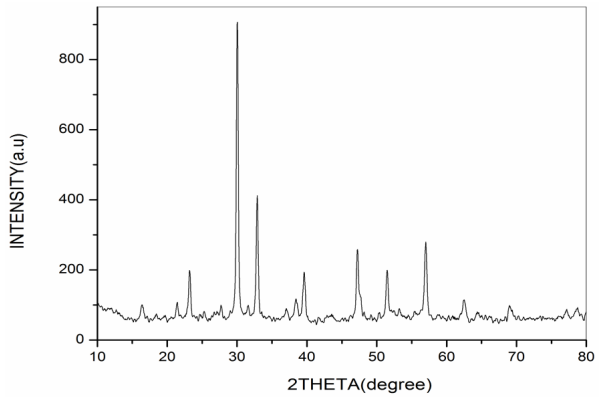

Fig 2: XRD spectra of barium bismuth titanate after milling of precursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 25 hours followed by annealing at 700°C for 8 hours

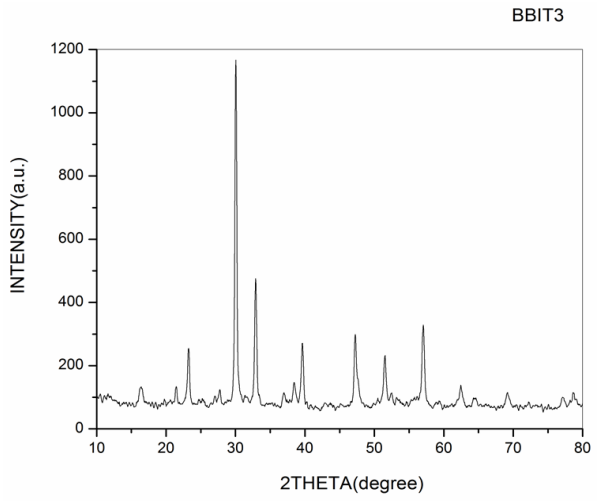

Fig 3: XRD spectra of barium bismuth titanate after milling of precursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 30 hours followed by annealing at 700°C for 6 hours

FTIR analysis is carried in the scan range of 450-4500cm^{-1} using KBr pellet as standard for reference. For all samples nature of graph is found to be similar. The bands observed in the range of 800-1100cm^{-1} is due to presence of Si-O-Si bonds. Approximately at about 1091cm^{-1}, 1166 cm^{-1} for Fig 4 is due to Si-O-Si bonds while such peaks are noted at about 1087 cm^{-1},1162 cm^{-1} and at about 1078 cm^{-1},1166cm^{-1} for Fig 5 and Fig 6 respectively. As per literature bands observed near 858, 900, 970, and 1036 cm^{-1} are due to the presence of Si–O–Si bonds.[11,12] The band at about 860 cm^{-1} is due to bending vibration of Si-O-Si linkage while bands observed at about 920 and 970 cm^{-1} are mainly due to symmetric stretching vibration of Si-O units. The spectra within 480-680 cm^{-1} represents Bi-O bonds. Absorption at about 500 cm^{-1} is due to BiO_6 distorted octahedral units.[11,12] In the present context, absorption spectra at about 542 cm^{-1}, 567 cm^{-1}, 563 cm^{-1}, 579 cm^{-1},617 cm^{-1},667 cm^{-1}, 675 cm^{-1} is mainly due to Bi-O bonds. Ti-O bonds are reflected at about 730 cm^{-1} which actually corresponds to asymmetric stretching of Ti-O tetrahedral units.

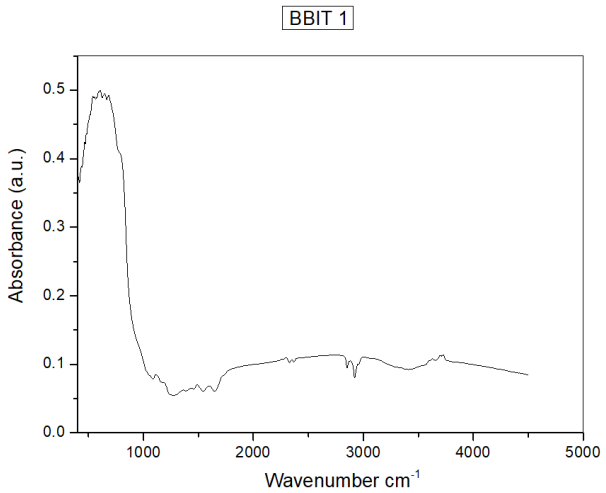

Fig 4: FTIR spectra of Barium Bismuth Titanate ($BaBi_4Ti_4O_{15}$) after milling of precursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 20 hours followed by annealing at 700°C for 10 hours

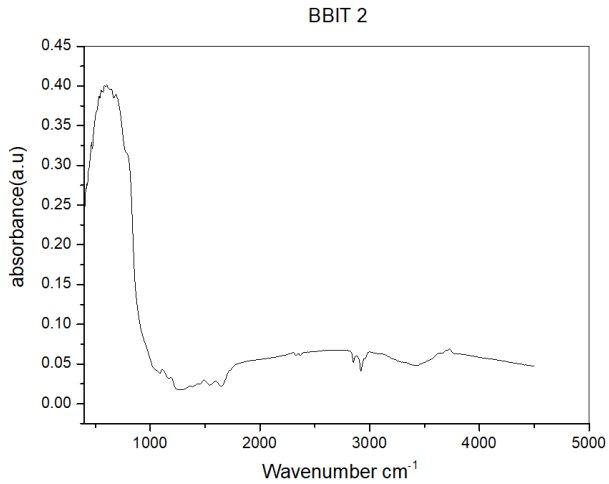

Fig 5: FTIR spectra of Barium Bismuth Titanate ($BaBi_4Ti_4O_{15}$) after milling ofprecursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 25 hours followed by annealing at 700°C for 8 hours

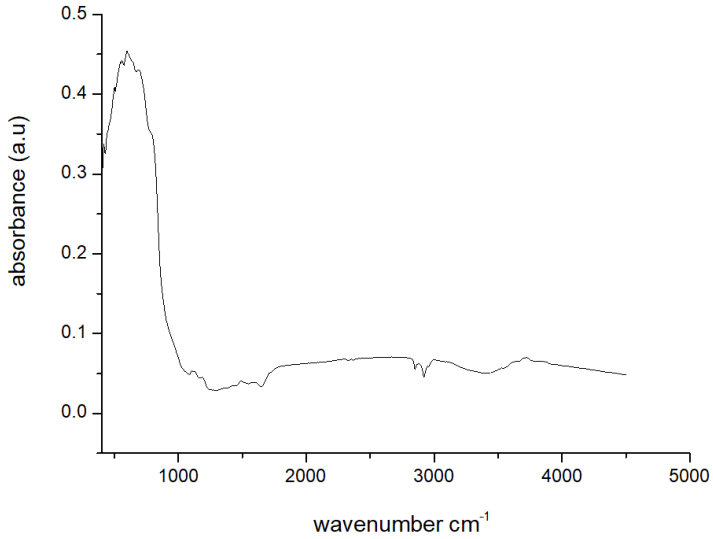

Fig 6: FTIR spectra of Barium Bismuth Titanate ($BaBi_4Ti_4O_{15}$) after milling of precursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 30 hours followed by annealing at 700°C for 6 hours

Figures 7-9 represents the morphological features studied by SEM followed by EDX analysis at certain specific zone. The morphology is noted to have agglomeration while the agglomerated chunks have irregular shape. Individual particulates are having spherical to irregular polygon shape with few interconnected pores. Particulates are about 0.5µ while rough patches are noted in some discreet portions. EDX analysis represents presence of Ba, Bi, Ti and O as elements required for the formation of barium bismuth titanate. EDX analysis in addition to FTIR bond stretching and vibration validates the phase analysis by XRD. Thus EDX provides the chemical analyses in designated morphological portions by means of presence of only desired peaks of the required elements.

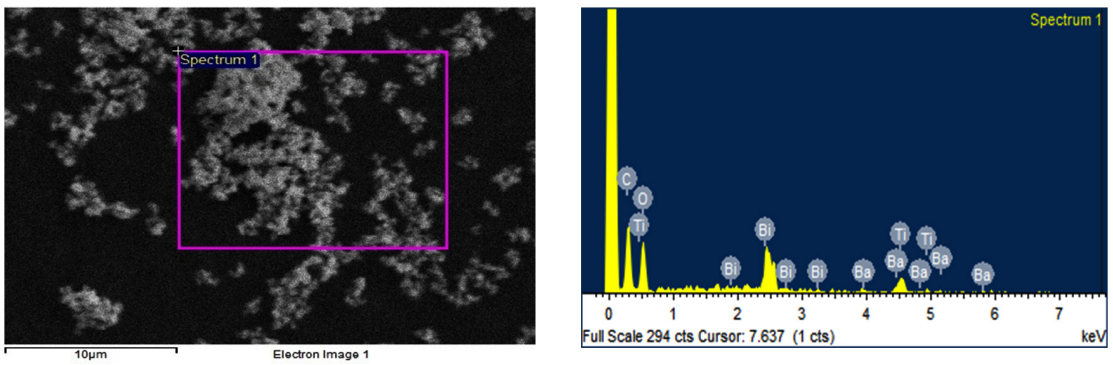

Fig 7: SEM-EDX image of Barium Bismuth Titanate after milling of precursors $BaO:Bi_2O_3:TiO_2$ in 1:2:4 molar ratio for 20 hours followed by annealing at 700°C for 10 hours

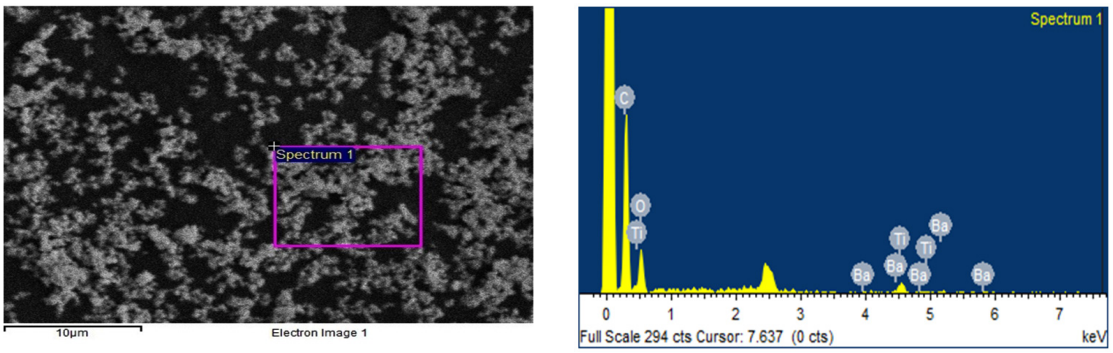

Fig 8: SEM-EDX image of Barium Bismuth Titanate after milling of precursors BaO:Bi_2O_3:TiO_2 in 1:2:4 molar ratio for 25 hours followed by annealing at 700°C for 8 hours

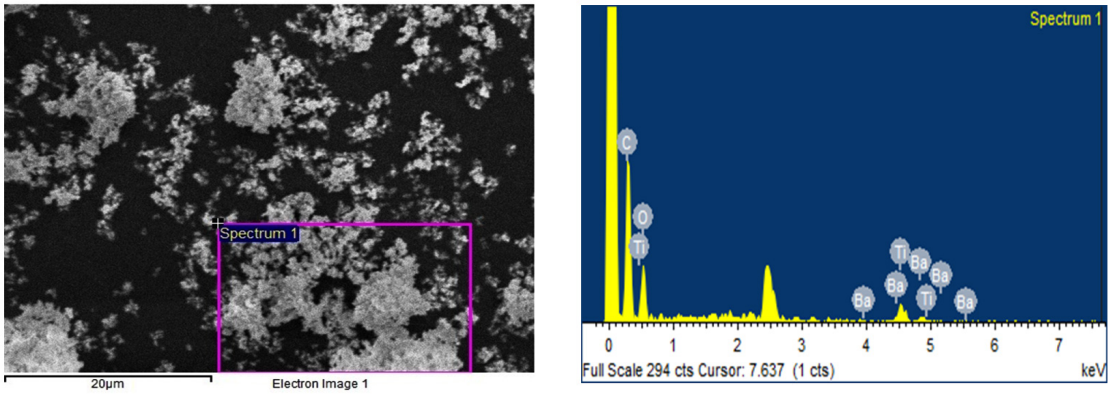

Fig 9: SEM-EDX image of Barium Bismuth Titanate after milling of precursors BaO:Bi_2O_3:TiO_2 in 1:2:4 molar ratio for 30 hours followed by annealing at 700°C for 6 hours

Conclusions

Modified Solid state route was carried to successfully synthesized barium bismuth titanate after undergoing agate mortar milling activation. Milling activation was carried for 20, 25 and 30 hours followed by annealing at 700°C for 10 hrs, 8 hours and 6 hours respectively. Crystallite size was estimated to be about 35.11nm, 35.08nm and 34.73 nm respectively. Crystallite size decreases with increase in milling time while the soaking period decreases at constant annealing temperature. FTIR analysis exhibits the required M-O coordinations of Si-O-Si bonds, Bi-O bonds and Ti-O bonds respectively. Morphology by SEM exhibits agglomeration tendency while individual particulates were noted to be spherical to irregular polygonal shape. EDX analysis confirms the presence of Ba, Bi, Ti and O as elements required for the formation of aurivillius compound.

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Conflict of Interest

There is no conflict of interest among authors.

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