Original Research

Structural Studies of BaTiO$_3$ Ferroelectric Material Prepared by Green Chemistry (Sol-gel) Method

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Abstract	Article Information
Nano particle Barium Titanate (BT) is the first ferroelectric ceramics and a good nominee for a variety of applications from large family of Perovskite. In this study BaTiO$_3$ was synthesised by using Sol-gel (green chemistry) method. It is environmental friendly method and has a significant influence on the structure and properties of BT. XRD patterns were indexed on the basis of tetragonal-BaTiO$_3$ phase. The microstructure of the samples was investigated by using Scanning electron microscope (SEM). The grain size range was 90 nm for the dried gel powder for the powder calcined at ≈ 1150°C. Infrared (IR) spectrum was recorded at room temperature. The absorption peak observed at 545 cm^{-1} found to be BT characterization peak.	
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INTRODUCTION

Barium titanate (BaTiO$_3$ abbreviated as BT) is a well-accepted Perovskite. BT is known as one of the best ferroelectric (FE) materials among the lead free community and important member among the ferroelectrics family of perovskite (ABO$_3$) compounds BT has been of great interest because of their proven superior electrical and optical properties. Many researchers have been attracted by its versatile crystal structures (Hsiang *et al.*, 1995; McCauley, 1998). FE thin films offer advantages over bulk for a number of applications, including non-volatile memories, dynamic random access memories, electro-optic switches, pyroelectric detectors, optical modulators etc. 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). BT was prepared by so many methods among these methods, sol–gel (Kamalasanan, 1993) processing has various advantages over other deposition techniques in terms of good homogeneity, stoichiometric control, high purity, low processing temperature, ability to produce uniform thickness with good conformal coverage, large area applications and compatibility with the already existing semiconductor technology (Antony Jeyaseelan, 2013; Jitianu *et al.,* (2003); Nowotny *et al.,* (1991); Chan *et al.,* 1976). Its natural excellence dielectric properties and potential for technological applications in ferroelectricity, microelectronics and optoelectronics, BaTiO$_3$ has attracted much credibility for variety of device applications (Dang-Hyok, 2006) and its being a lead-free ferroelectric ceramic and its environmentally friendly material and non-toxicity (Henning,1987). BT is also one of the most important electro-ceramic materials, since the discovery of its versatility in multilayer ceramic capacitors

(MLCC), thermistors, piezoelectric sensors, transducers, actuators, ferroelectric random access memories (FRAM), and energy storage devices. Doped barium titanate has found wide application in semiconductors, ultrasonic, piezoelectric devices, and has become one of the most important ferroelectric ceramics and electro-optic devices (Haertling, 1999; Zhou *et al.*, 1999). The main objective of the present study is to prepare BT for low temperature preparation and study the structural and grain morphology in detail.

MATERIALS AND METHODS

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 (Sreenu *et al.*, 2014) 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, ethylene glycol was used to modify the hydrolysis rate of the Ti precursor (Sreenu *et al.*, 2014). The stachometric amounts of barium nitrate (Ba(NO$_3$))$_2$ (Merck 99%) is taken in aqueous solution and titanium dioxide(TiO$_2$) dissolved in HF solution (Titanium peraxocomplex) is added to the solution. 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 calcinated at 1150^0C in furnace of oxygen atmosphere then the resultant powder was crushed and pressed into circular pellets of 10 mm diameter and ~ 1mm thickness. The detail synthesis protocol is in figure 1 and the possible chemical reactions are as follows:

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

In the present work, the temperature was applied to BT powder the sample was heated at a rate of 100^0 C /min to 1150^0 C and then cooled down to room temperature and held for 10 h. As a result a ceramic with relative density of 94% was obtained.

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$\circ$/min). The microstructure of the samples was investigated by using scanning electron microscope (Hitachi N3400 Japan). The FTIR patterns were acquired by using BRUKER OPTICS, Germany Model TENSOR 27 FTIR spectrometer from $4000 – 400$ cm^{-1}, using KBr pellet as a reference method.
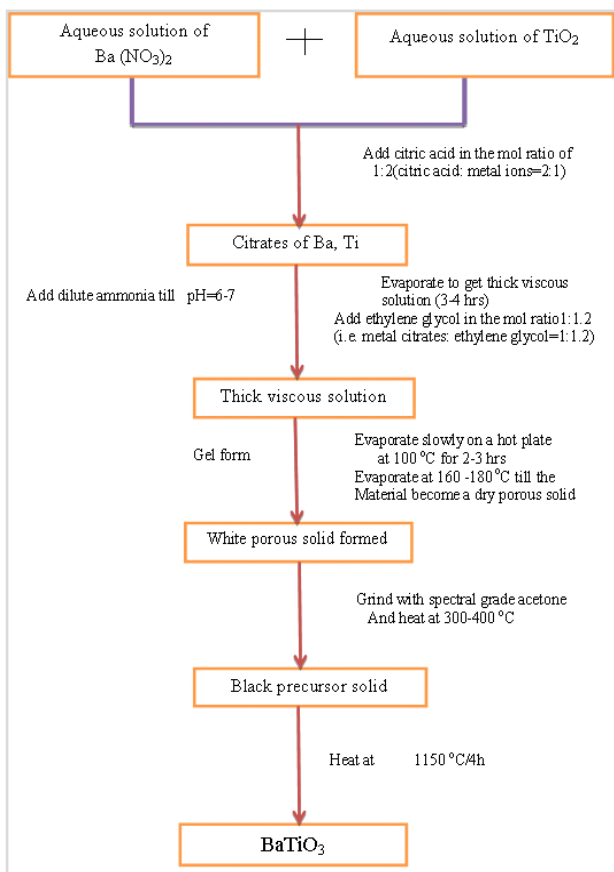

Figure 1: Sol-Gel Synthesis Flow Chart

RESULTS AND DISCUSSION

Structural Studies

Structural studies are carried out by X-ray diffraction using Cu-K$α$ radiation of $λ$=0.1542 nm at room temperature at a scanning rate of 2°/min over a wide $2θ$ range of 20° to 80°. Figure 2 shows room temperature X-ray diffraction (XRD) patterns obtained for BT. The

BaTiO$_3$ sample shows 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 insert figure 2. The splitting of (0 0 2) and (2 0 0) peaks clearly indicate the evidence for tetragonal phase. So, the present system shows the tetragonality in BaTiO$_3$, due to the different composition mechanism. All XRD peaks for BaTiO$_3$ were indexed on the basis of tetragonal structure and lattice parameters were calculated using POWD software by least square refinement method. The X-ray powder diffraction may also be used to measure the average crystal size from the peak broadening using the Scherrer formula (Patterson, 1939; Klug *et al.*, 1956). The values of lattice parameters for BaTiO$_3$ system are found to be a=b=3.9734Å; c=4.012 Å and cell volume, v = 63.3442 Å. (JCPDS No. 31-174). The average crystallite size of the nanoparticles was calculated from (101) peak of corresponding XRD peaks by using Scherrer's equation and found to be 95 nm the clear protocol is given in table no 1. The XRD pattern shows background in the region 20-400, this may be due to the reason that a thin layer of the nanopowder was spread on the glass slide placed in the sample holder for XRD studies which must have been resulted in large scattering of X-rays in this region.
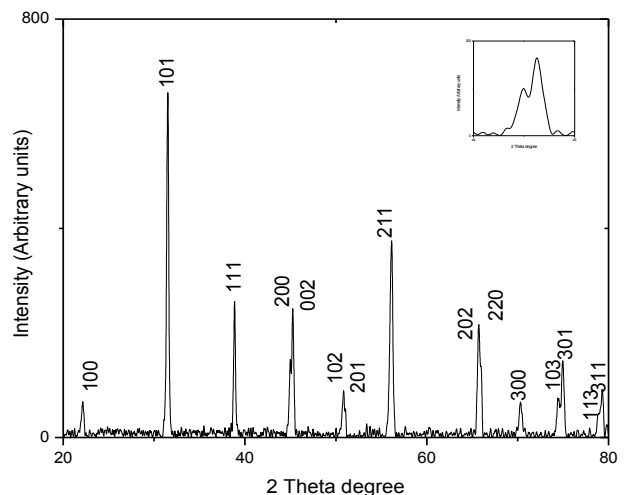

Figure 2: XRD-pattern of BaTiO$_3$

Table1: Sintering protocol, lattice parameters and crystal structure

Sample	Pre-sintering temperature ^oC for 4 hours	Final-sintering temperature ^oC for 4 hours	Lattice parameters	Volume A^{03}	Relative Density gm/cm^3	Crystalline size from XRD (nm)	Grain size from SEM (nm)
BaTiO$_3$	600	1150	a=b=3.9734 c=4.012	63.3442	94	95	90

Scanning Electron Microscopy (SEM)

The microstructure is shown in figure 3. Both the grain size and grain size dispersion are smaller. Faceted grains of about 90 nm were estimated by using line intersept method and grains boundaries appear clearly. Even though exact mechanism of the microstructure observed here is not well established, but it should be noted that the various features of microstructure in BT ceramics are dependent on the grain growth rate in the different planes (Lin *et al.*, 2000)). However, the sintering process and growth environment also play an important role in the formation (German, 1996).
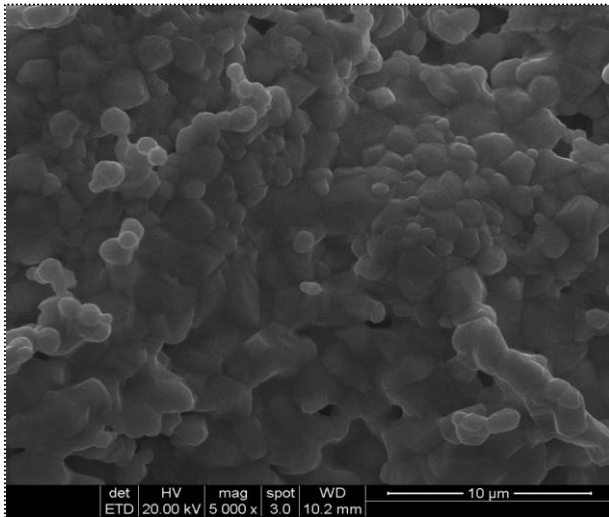
Figure 3: SEM pattern of BT ceramics

Energy Dispersive Spectroscopy (EDS) Analysis

To study the microstructure of ceramics and the distribution of constituents, selected specimens were extensively examined by SEM/EDS. As the analysis of a large number of individual grains by EDS for obtaining a comprehensive elemental distribution is tedious, elemental mapping over a microstructure was initially performed.

Elemental maps constructed utilizing the intensities of the characteristic X-rays of constituent elements provide a visual depiction of their relative spatial distribution in the region corresponding to the micrograph. Spot analysis ($<1\mu m^2$) over individual grains was subsequently performed for compositional analysis. Figure 4 shows EDS spectrum at Ti rich spots indicating the presence of Ba^{+2} formed by incorporating more than 20 at % Ba^{2+} in $BaTiO_3$. In the case of $BaTiO_3$ no smearing in Ti distribution and consequently Ti is always present together with 'Ba' in all specimens.
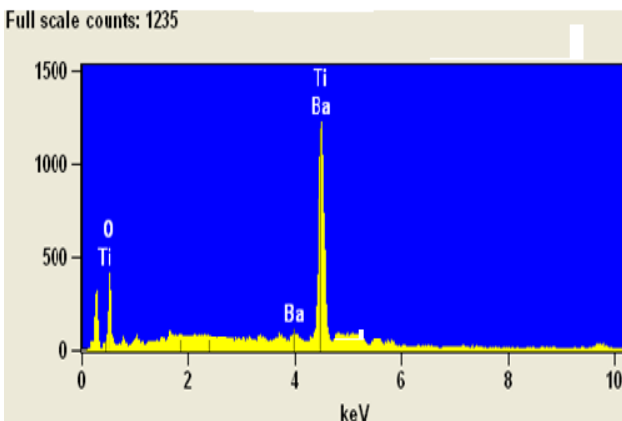

Figure 4: EDS of BT nanoparticle

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 5 shows FTIR spectra of BT, the observed absorption frequency, there are other two absorption bands. A low frequency band (below 400 cm^{-1}) is assigned to cationTiO_6 vibration. Another frequency band near 433 cm^{-1} is assigned to the Ti–O "bending" normal vibration as it were seen in above. The observed absorption frequency band, near 545 cm^{-1} is assigned to the Ti–O "stretching" normal vibration the band positions

is given in table no 2. This mode is very important because the direction of "stretching" normal vibration is along with that of spontaneous polarization in $BaTiO_3$ with tetragonal phase. Therefore the peaks observed in FTIR matches with that of XRD peaks position.
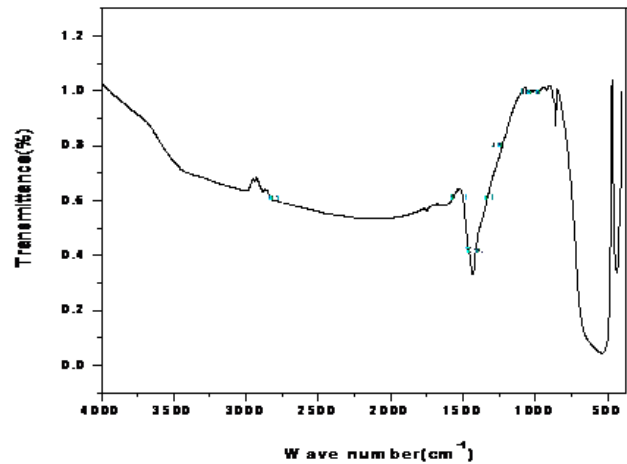

Figure 5: Infrared bond positions (cm^{-1}) of BT

Table 2: Infrared bond positions (cm^{-1}) of BT

Bond Position	Wave Number(cm^{-1})
Ba-O	1426
	1022
	980
Ti-O	700
	545
	433

CONCLUSIONS

The prepared sample of BT has been analysed by XRD, SEM, EDS and FTIR. The XRD showed single phase tetragonal structure by analysis, it showing splitting of peaks (2 0 0) and (0 0 2) of tetragonal in the 2θ range 44-46^0. We found that crystallite size was 95 nm from XRD using Scherer formula. In the study of lattice parameters, SEM results were revealed that has strong effect on the grain size. By careful observation of SEM photographs it may be presume that Ba-ion accumulated at grain boundaries and structure of grains is almost cubical shape. The limit cause the distance of Ti-O to become shorter or tilted or slanted, and it has been clearly observed the grain size of BT is 90 nm from SEM, the composition distribution completely existing. From the FTIR spectra analysis, it was observed that the pronounced peak at 545 cm^{-1} which is considered to be a characteristic feature of BT. The FTIR observation shown that as the wave number (k) of the sample increases there exist the bond formation of Ba-O showing high value of transmittance and when the wave number (k) decreases there is Ti-O bond formation lowering transmittance by increasing absorption.

ACKNOWLEDGEMENT

REFERENCES

Al-Shakarchi (2010). Dielectric properties of a BaTiO₃ ceramic prepared by using the freeze drying. *Journal of the Korean Physical Society* 57: 246-250.

Antony Jeyaseelan, A., Sruthi, S., Soma Dutta, (2013). Fabrication and characterization of epitaxial BaTiO₃ thin film employing platinum (1 1 1) template. *Advanced Materials Letters* 4(8): 632-636.

Chan. N.H. and Smyth. D.M. (1976), Defect Chemistry of BaTiO₃. *Journal of Electrochemical Society* 123: 1584-1585.

Dang-Hyok Yoon, (2006). Tetragonality of barium titanate powder for a ceramic capacitor application. Journal *of Ceramic Processing Research* 7(4): 343-354**.**

German R. M, (1996), Sintering Theory and Practice (Wiley, New York,), pp. 550.

Hsiang, H.I., Yen, F.S., Chang, Y.H. (1995). Effect of porosity on the dielectric properties of BaTiO₃ ceramics, *Japan Journal of Applied. Physics* 34: 1922-1925.

Hennings. D. (1987). Barium titanate based ceramic materials for dielectric use. *International Journal of High Technology Ceramics* 3: 91-111,

Haertling. G.H. (1999), Ferroelectric ceramics: History and technology. *Journal of American Ceramic Society* 82: 797-818.

Jitianu. A., Britchi. A., Deleanu. C., Badescu. V., Zaharescu M. (2003). Comparative study of the sol–gel processes starting with different substituted Si-alkoxides. *Journal of Non-Crystallographic Solids* 319: 263-279.

JCPDS (Joint Committee For Powder Diffraction Studies), No. 31-174

Kamalasanan. M.N., Deepak Kumar, N., Chandra. S. (1993). Structural, optical and dielectric properties of sol-gel derived SrTiO₃ thin films. *Journal of Applied Physics* 74: 679-686.

Klug, H.P. and Alexander A.E. (1956). Elements of X-ray Diffraction Procedures, John Wiley Inc, New York.

Lin, M.H., Chou. J.F. and Lu, H.Y. (2000). The rate-determining mechanism in the sintering barium titanate, *Journal of European Ceramic Society* 20: 517-526.

McCauley, D., Newnham. R.E., Randall, C.A. (1998). Intrinsic size affects in a barium titanate glass-*ceramic. Journal of American Ceramic Society* 81: 979-986.

Nowotny. J. and Rekas, M. (1991). Defect chemistry of BaTiO₃. *Solid State Ionics* 49: 135-154.

Patterson, A.L. (1939). The Scherrer Formula for X-Ray Particle Size Determination. *Physical Review* 56: 978-992.

Sreenu, K., Bhargavi, T. and Kebede Legesse Kabeta (2014), Characterization and Phase Transitions of Bi Doped BaTiO₃ Ceramics Prepared through Chemical Route *Science, Technology and Arts Research Journal* 3(1): 39-43.

Syed Mahaboob., Dutta. A.B., Swamynathan. G., Prasad, G., Kumar, G.S. (2005). Dielectric Properties of BaTiO₃ Based Lead Free Relaxor Prepared Through Conventional and Microwave Sintering. *Ferroelectrics* 326: 79-84.

Zhou. L., Vilarinho. P.M., Baptista J.L. (1999). Solubility of bismuth oxide in barium titanate. *Journal of American Ceramic Society* 82: 1064-1066.