Wet chemical synthesis and investigations of structural and dielectric properties of BaTiO$_3$ nanoparticles

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Abstract In the present study, Barium Titanate (BaTiO$_3$) nanoparticles were synthesized using one of the best route chemical method that is sol-gel auto combustion method. The structural and dielectric properties were investigated by powder X-ray diffraction (XRD), LCR meter and the results are reported herein. The phase purity and structural determination was carried by XRD technique at room temperature. The analysis of XRD patterns revealed of formation of single phase tetragonal structure. The lattice parameters ‘a’ and ‘c’ were obtained using XRD data and obtained lattice parameters matches with reported value. Average crystallite size was determined using Debye–Scherrer’s formula and is found to be 6.4 Å indicating nanocrystalline nature. Dielectric properties like dielectric constant and dielectric loss tangent was investigated using LCR-Q meter method at varying frequencies. Both dielectric constant and dielectric loss tangent decreases with increasing frequencies. The PE characteristics and other studies are in progress.

1. Introduction

Barium Titanate (BaTiO$_3$) is a member of a large family of compounds with the general formula ABO$_3$ which has perovskite structure. Barium Titanate can be prepared using different methods. The synthesis method depends on the desired characteristics for the end application and the method used has a significant influence on the structure and properties of Barium Titanate. BaTiO$_3$ have been attracted considerable interest for a wide variety of applications. It has a perovskite structure that possesses a high dielectric constant [1] and widely used in multilayer ceramic capacitors (MLCCs), dynamic random access ferroelectric memories (DRAMs) [2, 3] Doped barium titanate has found wide application in semiconductors, PTC thermostats and piezoelectric devices, and has become one of the most important ferroelectric ceramics. The properties of BaTiO$_3$ have been reported in a number of papers. Barium titanate is a member of a large group of compounds which is called the perovskite family. Ceramic materials with a perovskite structure are very significant electronic materials. [4] It is well known that the properties of BaTiO$_3$ powders and ceramics strongly depend on the synthesis route and sintering regime.[5] It is an important ceramic material for electronic and memory devices. The perovskite structure of BaTiO$_3$ makes it a candidate to host different dopant ions with different sizes. Previously, it has been reported that the rare earth dopant can
greatly modified the electrical properties of BaTiO3. Trivalent rare earth cation have the ability to substitute into either A-site (Ba2+) or B-site (Ti4+) of BaTiO3 because of their moderate ionic radius between Ba2+ and Ti4+ ions [6]. The perovskite-type BaTiO3 ceramics shows a ferroelectric state below the temperature of 400K, at which the crystal structure changes from a cubic to tetragonal one in a first-order-type structural transition [9]. In the recent year wet chemical methods such as sol-gel auto-combustion, chemical method have been used to produce nanopowder of BaTiO3 [7]. The advantages of this technique are that it produces powder of nano-scale dimension, more homogeneous, highly lour and better control over stoichiometry [8]. In the present study, we report the low temperature synthesis of BaTiO3 using sol-gel auto-combustion method and results of the investigation of structural, infrared and dielectric properties are reported in this work.

2. Experimental

**Materials:**
Analytical grade barium nitrate hexahydrate (Ba (NO3)2•6H2O, 99%, Sigma Aldrich ), tetra butyl titanate (Ti(OC4H9)4, 99.9%, Alfa Aesar), • 4H2O), citric acid (C6H8O7, 99.57%, Sigma Aldrich ) ethanol (C2H5-OH, 99% ,Sigma Aldrich) and ammonium hydroxide (NH4OH, 99%) were used without further purification.

**Preparation of BaTiO3 nanoceramic**
BaTiO3 nanoceramic was synthesized by safe and easier sol-gel auto combustion technique. Firstly, tetra butyl titanate solution diluted with ethanol was added into the aqueous solution of citric acid. After being stirred at 80 °C for 1 h, a yellowish transparent liquid was obtained which is marked as solution A. At the same time, barium nitrate was dissolved into deionized water and mixed to form an aqueous solution, which is marked as solution B. Subsequently, solutions A and B were poured together. At the same time the pH value was adjusted to be 7 (pH= 7) using ammonia till a transparent liquid was achieved. The synthesis protocol was followed by a continuous stirring for 3 hrs. on magnetic hot plate stirrer to increase the viscosity of solution gradually and then a stable transparent sol was formed. Continuous heating of ~110 °C initiates the gel formation. Under the constant stirring and heating, viscous gel transforms into a dry gel. The gel formed from metal nitrates and citric acid exhibited self-propagating combustion behaviour, and the entire combustion process was done in few seconds. The obtained powder was dried, crushed and was sintered at 1100°C for 6 h in a muffle furnace in order to get the nanocrystalline powders.

**Characterization**
- The X-ray diffraction (XRD) pattern of prepared pure BaTiO3 by sol Gel Auto combustion Method was obtained using Bruker D8 advance diffractometer at room temperature. Crystalline phases of the samples was examined by and recorded using Cu-Kα radiation (λ = 1.54182 Å) in the 2θ range 20°- 80° with step size 0.01°and time/step 2s.
- Using the LCR-Q meter (Hioki 3532–50, Japan) the dielectric properties of the sample was measured as a function of frequencies in the range 50 Hz - 5 MHz at room temperature.
- The infrared optical properties of dried gel powder was recorded on Bruker spectrophotometer using KBr as a reference material in the wave number range 4000–60cm⁻¹

3. Results and Discussion

**X-ray diffraction (XRD)**
Fig. 2 show X-ray diffraction (XRD) patterns of powder of BaTiO3 samples. A close examination of XRD patterns reveals the formation of single-phase compound. No extra peak has been identified in the XRD patterns. All the diffraction peaks pure of BaTiO3 are well indexed. The sample shows the tetragonal structure with P4mm space group. The XRD patterns well matches with JCPDS 79-2264.
Fig. 2 XRD patterns of BaTiO$_3$

The lattice parameters ‘a’ and ‘c’ BaTiO$_3$ was calculated using the following formula for tetragonal structure[7],

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Where $d$ is interplanar spacing ‘a’ and ‘c’ lattice constant, (hkl) are Miller indices.

The values of lattice parameters of ‘a’ and ‘c’ are listed in table 1. Further c/a ratio was also calculated and its values are listed in table 1. The ratio c/a is more than one which indicates the tetragonal structure of BaTiO$_3$.

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + l^2}{a^2} \right) + \frac{l^2}{c^2}$$

The other structural parameters like X-ray density, unit cell volume and lattice strain were also calculated using XRD data. The unit cell volume (V) was calculated using following relation[11],

$$V = a^2c$$

The values of unit cell volume are given in table 1.

Table 1 Lattice parameters (a and c), unit cell volume (V), lattice strain ($\varepsilon$)), obtained by XRD of BTM nanoparticles showing tetragonal phase (T) structure.

| X | Structure | a (Å) | c (Å) | c/a | V (Å$^3$) | $\varepsilon$ |
|---|-----------|------|------|-----|----------|----------|
| 0.00 | T         | 3.989 | 3.994 | 1.026 | 63.266   | 0.076    |

The x-ray density ($\rho_x$) was determined by the following relation[18] and obtained values are listed in table 2.

$$\rho_x = \frac{ZM}{N_AV}$$

Where, $Z$ is the number of formula units in unit cell, $M$ is molecular mass of the sample and $N_A$ is the Avogadro’s number. The X-ray density can be observed from table 2. The lattice strain ($\varepsilon$) was also calculated by using relation [19].

$$\varepsilon = \frac{\beta \cos \theta}{4}$$
Where \( \varepsilon \) is the root mean square value of lattice strain, \( \beta \) is full width of peak half maxima and \( \theta \) is peak position. The crystallite size \( (t) \) was determined by using Debye-Scherrer’s formula\[20\],

\[
 t = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Where \( \lambda \) is wavelength of Cu-K\( \alpha \) radiation, \( \beta \) is the full width of the half maximum and \( \theta \) is the Bragg angle. As the crystallite size found to be in the range of 5-8 nm indicates nanocrystalline nature of BaTiO\(_3\).

Table 2. 2θ (Degree), FWHM, X-ray density, average crystallite size (t), obtained by XRD of BTM nanoparticles with respect to composition

| Composition (x) | 2θ (110) | FWHM | \( \rho_x \) (g/cc) | \( T \) (Å) |
|-----------------|---------|------|-----------------|--------|
| 0.00            | 31.697  | 0.2054 | 6.119           | 6.493  |

**FT-IR studies**

Fourier transform Infrared spectroscopy (FT-IR) of the samples under investigation recorded in the range 400-4000 cm\(^{-1}\) at room temperature. The spectra shows four prominent bands near 600 cm\(^{-1}\), 1500 cm\(^{-1}\), 2335 cm\(^{-1}\)and 3700 cm\(^{-1}\). The first absorption band (\( \nu_1 \)) near 600 cm\(^{-1}\) corresponds to Ti-O stretching vibrations in the samples. The second absorption (\( \nu_2 \)) band near to 1500 cm\(^{-1}\) and this absorption band is corresponds to the deformation mode of absorbed water (H\(_2\)O) molecules, assigned to the bending vibrations. The third absorption (\( \nu_3 \)) band around 2335 cm\(^{-1}\) corresponds to C-O stretching vibrations. The fourth absorption (\( \nu_4 \)) band around 3700 cm\(^{-1}\) has been assigned to O-H stretching (symmetric and asymmetric) vibrations hydrogen bonded OH groups. Table 3 represents the peak position corresponds to absorption bands. Further it is also noticed from FTIR spectra that in BaTiO\(_3\) only shifting in absorption band is observed.

![FT-IR spectra of BaTiO\(_3\)](image)

**Table 3** Absorption bands and its position with respected to corresponding bonds

| Composition (x) | \( \nu_1 \) | \( \nu_2 \) | \( \nu_3 \) | \( \nu_4 \) |
|-----------------|---------|---------|---------|---------|
| 0.00            | 599     | 1422    | 2337    | 3728    |
| Attributed to   | Ti-O    | H2O     | C-O     | O-H     |
Dielectric studies

The dielectric properties of BaTiO3 was studied at room temperature using LCR-Q meter in the frequency range 50 Hz to 5 MHz. The real part of dielectric constant $\varepsilon'$ was calculated by using following relation[21],

$$
\varepsilon' = \frac{Ct}{\varepsilon_0 A}
$$

Where, C is the capacitance of pallet, t is the thickness of the specimen, A is the area of cross-section of the pallet and $\varepsilon_0$ is the permittivity of free space. Fig. 5 represents the variation of dielectric constants as a function of frequency. It is observed from fig. 5 that dielectric constant decreases with increase in frequency. Fig. 6 and fig. 7 represent variation of dielectric loss $\varepsilon''$ and dielectric loss tangent (tan $\delta$). Similar to dielectric constant, dielectric loss and dielectric loss tangent decreases with increasing frequency.

![Fig. 5 Variation of dielectric constant ($\varepsilon'$) with frequency at room temperature of BaTiO3 nanoceramics](image)

![Fig. 6 Variation of dielectric loss ($\varepsilon''$) with frequency at room temperature of BaTiO3 nanoceramics](image)
Conclusion

- Highly pure BaTiO$_3$ powder has been obtained successfully synthesised using sol-gel auto-combustion method.
- The BaTiO$_3$ powder shows the nanocrystalline and high chemical homogeneity nature as the crystallite size found is in the range of 5-8 nm.
- The XRD patterns confirms a single phase tetragonal structure with space group P4mm is obtained.
- The characteristic feature of ferroelectric Barium titanate obtained through the FT-IR spectra shows four absorption bands at around 600 cm$^{-1}$, 1500 cm$^{-1}$, 2335 cm$^{-1}$, and 3700 cm$^{-1}$.
- With increasing frequency the parameters dielectric constant, dielectric loss and dielectric loss tangent were found decreasing.

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