Barium titanate microspheres by low temperature hydrothermal method: studies on structural, morphological, and optical properties

D. Kothandan*, R. Jeevan Kumarb and K. Chandra Babu Naidu

*Department of Physics, Sreenivasa Institute of Technology and Management Sciences, Chittoor, India; bDepartment of Physics, S. K. University, Anantapuramu, India; cDepartment of Humanities and Sciences, Srinivasa Ramanujan Institute of Technology, Anantapuramu, India

ABSTRACT
The barium titanate (BT) microspheres were synthesized via the low temperature hydrothermal technique. The X-ray diffraction pattern confirmed the formation of cubic perovskite structure of the material. The average crystallite size \( (D_p) \) was found to be of 21 nm using the Scherrer method. The Williamson–Hall plot was drawn for evaluating the micro-strain and crystallite diameter. The relation between micro-strain \( (\varepsilon) \) and \( D_p \) was illustrated as a function of diffraction angle \( (2\theta) \). The morphology was analyzed by field emission and transmission electron microscopy. The results expressed the formation of microspheres. In addition to these, the optical bandgap \( (E_{\text{gap}}) \) and maximum absorption wavelength \( (\lambda_{\text{m}}) \) were achieved to be of 3.23 eV and 340 nm, respectively. The presence of metal oxide bonds (M-O) was observed which in turn attributes the formation of cubic structure.

1. Introduction
Nanoparticle-synthesis techniques have got more importance than the bulk-synthesis technique owing to their potential applications in biomedical sciences, drug delivery systems, sensors, nanofibers, carbon nanotubes, quantum dots, photocatalysis, dielectric, ferroelectric, and piezoelectric properties [1].

In general, the barium titanate (BT) is a promising dielectric material and showed tremendous applications as multilayer ceramic capacitors due to decrease of particle size [2]. The reduction in particle size can be attributed to the usage of low-operating temperatures while conducting the synthesis part of work. The significance behind the low temperature synthesis techniques was achieving the high purity, homogeneous, and ultrafine nanoparticles [2]. Several researchers prepared the BT nanoparticles via distinct methods such as hydrothermal [2], sol-gel [3], micro-emulsion [4], polymeric precursor [5] and microwave heating [6]. All the above-stated techniques focussed on the structural, morphological, Raman & IR-spectra, UV-visible spectra, dielectric, and ferroelectric properties. More recently Selvarajan et al. [7] prepared the piezoelectric BT nanoparticles and proposed that it can be used as an active biosensor for the biomolecular detection via the conventional solid-state reaction method. In addition to these, Singh et al. [8] experimentally showed that the perovskite BT thin film is an effective material for LPG sensor. According to the literature survey, the BT nanoparticles were mainly focussed to reveal the biomedical and sensor applications. Therefore, in the current investigation, the authors focussed to elucidate the structural, morphological, and optical properties of BT microspheres.

2. Experimental procedure
In order to synthesize the BT nanoparticles, the starting materials were chosen as Ba (NO\(_3\))\(_2\) and TiO\(_2\) (each of 99.9% purity, Sigma-Aldrich). These precursors were mixed together after taking their stoichiometric ratio. The whole mixed precursors were transferred to glass beaker. Furthermore, distilled water was added to the precursors in the ratio of 1:4 (mixed precursors (gm): distilled water (ml)) and the resultant solution was kept on a magnetic stirrer. A stirring rate of 500 rpm was maintained in order to stir the solution. Later NaOH solution was slowly added, and the p\(^{\text{H}}\) value reached to 11.3. Furthermore, this solution was transferred to 300 ml Teflon bowl inserted in an autoclave. The sealed autoclave was kept in a hot-air oven at an operating temperature of 130°C/6 hours. After completion of the reaction, the autoclave was slowly cooled to room temperature. The final BaTiO\(_3\) nanoparticles were removed from the Teflon-lined autoclave and washed with acetone and distilled water for 10 to 12 times until the p\(^{\text{H}}\) was reduced to 7. Later it was heated at 60°C C/2 hour. The final BT new particles were removed and characterized for various
characterized techniques such as X-ray diffraction method field emission scanning and transition electron microscopy. In addition, the Fourier transform infrared spectroscopy (FTIR), UV-visible techniques were used to find the presence of metal oxide bands and the optical energy band gap. The flowchart for the experimental procedure is shown in Figure 1(a).

3. Results and discussions

3.1. XRD analysis

The diffraction pattern of BT nanoparticles is depicted in Figure 1(b). It can be seen that the barium copper titanate (BCT) nanoparticles exhibit the cubic perovskite structure pertaining the reflection planes as indicated in Figure 1(b). These reflection planes are in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) data of file number: 89–2475. Among these planes, the 110 plane at 31.55° revealed the maximum intensity. No secondary peaks are observed in BT structure. The average crystallite size ($D_p$) is evaluated with the help of average full-width at half-maxima (FWHM) of reflection planes using the Debye–Scherrer equation [9],

$$D_p = \frac{k\lambda}{\beta \cos \theta}$$

where $\beta$ is full width half maxima, $\lambda$ is wave length of CuK$_\alpha$ radiation (0.1542 nm), $\theta$ is diffraction angle, and “k” is a numerical constant which is equal to 0.9 for a spherical atom. The results are repeated in Table 1. It is clear from the table that the crystal size is varying from 4 to 45 nm. The average $D_p$ is calculated to be 21 nm.

Figure 1. (a) Flow chart of sample preparation. (b) The diffraction pattern of BT nanoparticles.
Figure 2 depicts the variation of D_p and micro-strain as a function of diffraction angle. It is very clear from the figure that there exists a reciprocal relationship between micro-strain and D_p. Similar kinds of observations were previously reported in the literature \cite{10}. In addition, the lattice constant (a) is calculated after finding the inter-planer spacing (d) and miller indices (hkl) by using the following formula \cite{10}:

\[ a = d(1^2+k^2+l^2)^{1/2} \]  

(2)

The lattice parameter is found to be 4.007 Å. This value is greater than the reported lattice constant of 3.972 Å for bulk BT material \cite{11}. The X-ray density (D_x) is evaluated using the formula ZM/Na^3, where “Z” is the number of molecules per unit cell (Z = 8), “M” is the molecular weight of the composition, “N” is Avogadro’s number (6.023 x 10^23), and “a” is the lattice parameter \cite{10}. The numerical value of D_x is observed to be 6.022 g/cm^3 which is larger than the D_x of bulk BT of 5.427 g/cm^3 \cite{11}. This may be attributed to the high homogeneity of prepared BT nanoparticles. Moreover, the structural parameters such as inter-planer spacing (d), FWHM, micro-strain (ε), miller indices (hkl), and dislocation density (ρ) are listed in Table 1 as a function of diffraction angle. The inter-planer spacing is decreasing with increase of 2θ angle. In addition, the dislocation density is a parameter that evaluates the defects per unit area of the sample. The smaller value of ρ indicates the low porous structure of BT nanoparticles and vice versa. In the current study, the average ρ is \~7.96 x 10^{15} m^{-2}. The micro-strain at an average of all diffraction angles is noticed as 0.0044. The specific surface area (S) is a significant physical parameter for nanoparticles and is computed using the relation 6000/\(D_pD_x\) where the symbols have their usual meaning \cite{12}. In this study the S is achieved to be \~50 m^2/g. This kind of high value of S can be attributed to the smallest value of D_p when compared with bulk materials. This larger S value in turn affects the electrical, optical, and morphological properties of nanoparticles.

Williamson–Hall (W–H) plot (as shown in Figure 3) is drawn for \(\beta \cos \theta\) versus \(4 \sin \theta\) in order to evaluate micro-strain (ε) and crystallite size (D_p) using the following relation \cite{13},

\[ \beta \cos \theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin \theta \]  

(3)

where slope of straight line offers micro-strain while D_p is associated to intercept parameter. This provides the correlation between strain and size of the crystallite. The results from W–H plot express that the strain (0.0041) is almost consistent with the Scherrer strain from diffraction pattern. The average D_p is of order of 19.5 nm which is almost in agreement with the Scherrer size.

### 3.2. Surface morphology

The surface morphology of BT nanoparticles is analyzed by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The FESEM photographs of BT nanoparticles are showed in Figure 4(a).

From Figure 4(a), it is noticed that BT shows well-defined spherical grains. The grain size (G_a) is determined using linear intercept method \cite{12},

\[ G_a = 3L/2MN \]  

(4)

### Table 1. The data on structural and physical parameters of BT nanoparticles.

| 2θ (°) | FWHM β (°) | d (Å) | ε    | D_p (nm) | hkl     | ρ (m⁻²) |
|-------|------------|-------|------|--------|---------|---------|
| 22.173| 0.221      | 4.006 | 0.0049| 39     | 100     | 6.57E+14|
| 31.548| 0.175      | 2.834 | 0.0027| 45     | 110     | 4.94E+14|
| 38.861| 0.21       | 2.316 | 0.0026| 38     | 111     | 6.93E+14|
| 45.174| 0.441      | 2.006 | 0.0046| 21     | 200     | 2.27E+15|
| 50.861| 0.546      | 1.794 | 0.0050| 17     | 210     | 3.46E+15|
| 56.172| 0.37       | 1.638 | 0.0030| 24     | 211     | 1.74E+15|
| 65.737| 0.464      | 1.419 | 0.0031| 20     | 220     | 2.5E+15  |
| 70.3  | 0.869      | 1.338 | 0.0054| 12     | 300     | 6.94E+15|
| 74.737| 0.777      | 1.269 | 0.0044| 14     | 310     | 5.1E+15  |
| 79.05 | 0.951      | 1.211 | 0.0050| 12     | 311     | 6.94E+15|
| 83.425| 0.472      | 1.158 | 0.0023| 21     | 222     | 2.27E+15|
| 87.488| 2.119      | 1.114 | 0.0142| 4      | 220     | 6.25E+16|

Figure 2. The variation of micro-strain and D_p of BT nanoparticles.

Figure 3. The W–H plot of BT nanoparticles.

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where “L” is the line length, “N” is the number of grains intercepting the test line, and “M” is the magnification. The “G_a” is found to be altering between 196 to 235 nm. This confirms the presence of microspheres. The energy dispersive X-ray analyzer (EDAX) (Figure 4(b)) reveals the presence of Ba, Ti and O elements.

TEM generally provides the information about the existence of nanoparticles. The TEM images of BT nanoparticles are shown in Figure 5. It is seen from Figure 5 that all BT nanoparticles are of spherical in shape. The particle size is varying between 183 to 207 nm. In TEM images a weak agglomeration is identified.

3.3. Optical properties

3.3.1. FTIR analysis

The FTIR absorption spectra of synthesized BT nano-particles are recorded in the range of 4000 to 400 cm\(^{-1}\) as depicted in Figure 6. Two kinds of

Figure 4. (a) The FESEM photos of BT nanoparticles. (b) The EDAX of BT nanoparticles.

Figure 5. The TEM photos of BT nanoparticles.
metal oxide (MO) stretching vibrations are detected in the range of 400 to 520 cm$^{-1}$. This ensures the formation of perovskite BT structure. A narrow absorption band is noticed around 412 cm$^{-1}$ while broad absorption band around 513 cm$^{-1}$. These two absorption bands reflect the presence of Ba-O and Ti-O bonds. In addition few peaks are detected at 1122 cm$^{-1}$, 1360 cm$^{-1}$, and 2853 cm$^{-1}$. The peaks at 1124 cm$^{-1}$ and 1362 cm$^{-1}$ are associated to the bending vibrations of oxygen and hydrogen (O-H) that can be observed from the absorption of O-H by the BT nano-particles [13]. Another absorption peak is at 2852 cm$^{-1}$ is attributed to the intra-molecular stretching modes that occur from distinct properties of hydrogen bonding [13] within the frame network of perovskite structure.

3.3.2. UV-visible spectral analysis

The difference reflectance spectrum (Figure 7) is recorded in the range of 500–2500 nm for evaluating optical band gap of powder samples. The Kubelka–Munk function of reflectance $F(r)$ is used to determine the band gap [12].

$$F(r) = \frac{(1 - r)^2}{2r} \quad (5)$$

The absorption coefficient ($\alpha$) is directly proportional to $F(r)$ and hence an equation to find band gap can be written as follows [12],

$$(\alpha h\nu)^n = m (h\nu - E_g) \quad (6)$$

where “$m$” is energy-independent constant that depends on transition probability, “$E_g$” is optical band gap energy, “$n$” depends on the kind of transition, i.e. $n = 2$ for direct transition, $2/3$ for direct forbidden transition, $1/2$ for indirect transition, and “$h\nu$” is photon energy. In this study, $n = 2$ is taken for the direct transition [12]. The $E_g$ value is considered as extrapolated tangent value towards x-axis for $(\alpha h\nu)^2$ versus photon energy $h\nu$ (eV) plot as $\alpha$ tends to zero.

The maximum absorption wavelength ($\lambda_m$) for BT nanoparticles is shown in Figure 8. It is observed from figure that the $\lambda_m$ value is acquired to be 340 nm for the BT nanoparticles. The optical band gap is found to be 3.23 eV and is in consistent with previously reported data [8].

4. Conclusions

The BaTiO$_3$ nanoparticles were prepared by hydrothermal technique. The diffraction pattern revealed the perovskite BT cubic structure. The size of spherical grains is observed to be altering between 193 to 235 nm. The TEM study shows the agglomerated spherical nanoparticles. The presence of metal oxide bonds (M-O) were evaluated from Fourier transform infrared spectra. The UV-visible spectrum attributes the optical band gap energy of 3.23 eV.
Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Ciofania G, Ricotti L, Canalec C, et al. Effects of barium titanate nanoparticles on proliferation and differentiation of ratmesenchymal stem cells. Colloids Surf B Biointerfaces. 2013;102:312–320.

[2] Lu SW, Lee BI, Wang ZL, et al. Hydrothermal synthesis and structural characterization of BaTiO$_3$ nanocrystals. J Cryst Growth. 2000;219:269–276.

[3] Frey MH, Payne DA. Grain-size effect on structure and phase transformations for barium titanate. Phys Rev B. 1996;54:3158–3168.

[4] Wang J, Fang J, Ng SC, et al. Ultrafine Barium Titanate powders via microemulsion processing routes. J Am Ceramic Soc. 1999;82:873–881.

[5] Cho WS. Structural evolution and characterization of BaTiO$_3$ nanoparticles synthesized from polymeric precursor. J Phys Chem Solids. 1998;59:659–666.

[6] Ma Y, Vileno E, Suib S, et al. Synthesis of tetragonal BaTiO$_3$ by microwave heating and conventional heating. Chem Mater. 1997;9:3023–3031.

[7] Selvarajan S, Alluri NR, Chandrasekhar A, et al. Unconventional active biosensor made of piezoelectric BaTiO$_3$ nanoparticles for biomolecule detection. Sens Actuators B. 2017;253:1180. DOI:10.1016/j.snb.2017.07.159

[8] Singh M, Yadav BC, Ranjan A, et al. Synthesis and characterization of perovskite barium titanate thin-film and its application as LPG sensor. Sens Actuators B. 2017;241:1170–1178. DOI:10.1016/j.snb.2016.10.018

[9] Maddaiah M, Naidu KCB, Rani DJ, et al. Synthesis and characterization of CuO-doped SrTiO$_3$ ceramics. J Ovonic Res. 2015;11:99–106.

[10] Chandra Babu Naidu K, Madhuri W. Microwave processed NiMg ferrite: studies on structural and magnetic properties. J Magn Magn Mater. 2016;420:109–116.

[11] Reddy VN, Babu Naidu KC, Subbarao T. Structural, optical and ferroelectric properties of BaTiO$_3$ ceramics. J Ovonic Res. 2016;12:185–191.

[12] Chandra Babu Naidu K, Madhuri W. Microwave assisted solid state reaction method: investigations on electrical and magnetic properties NiMgZn ferrites. Mater Chem Phys. 2016;181:432–443.

[13] Chandra Babu Naidu K, Madhuri W. Hydrothermal synthesis of NiFe$_2$O$_4$ nanoparticles: structural, Morphological, optical, electrical and magnetic properties. Bull Material Sci. 2017;40:417–425.