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Synthesis and Characterization of Barium Titanate Nanopowders by Pechini Process

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Abstract

Barium titanate ($BaTiO_3$) is the first known ferroelectric ceramics and a suitable candidate for various applications due to its unique dielectric, ferroelectric and piezoelectric properties. It is well known that $BaTiO_3$ powder features strongly depend on the synthesis route and heat-treatment conditions. In the present study, $BaTiO_3$ nanoparticles have been synthesized via the Pechini method, using barium acetate and an aqueous solution of titanium(IV) (triethanolaminato) isopropoxide. The starting materials are stable in an aqueous environment, and $BaTiO_3$ can be efficiently prepared at an industrial scale. The structural properties of $BaTiO_3$ were characterized by X-ray diffraction (XRD), Rietveld refinement, scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FT-IR). XRD and Rietveld refinement studies revealed that $BaTiO_3$ has a cubic structure with a space group of *Pm-3m* (#221). As estimated by the Scherrer formula, the average crystallite size was accurately determined to be 51.9 nm for the calcined temperature at 800ºC. The SEM micrographs of powder showed that the $BaTiO_3$ grains are round-shaped, and the average grain size is observed about 40-90 nm.

Keywords: Barium titanate, Pechini, Rietveld, XRD

1. Introduction

In the early 1940s, after the discovery of barium titanate, which is the first oxide compound in perovskite structure with ferroelectric behavior, has been used for an extensive range of scientific and industrial applications, like piezoelectric infrared sensors, capacitors (electrical storage circuit element), ultrasonic transducers (the electrical device that converts electrical energy into mechanical motion). Because of its versatility, barium titanate has enhanced one of the most relevant electro-ceramic elements among ferroelectric materials. Its ferroelectric characteristics are connected with three structural phase transitions. Three-phase transitions are potential in the $BaTiO_3$, endowing with to temperature: from orthorhombic to tetragonal (-90ºC to 5ºC), tetragonal ferroelectric (5ºC to 120ºC) to cubic paraelectric (T>120ºC) structure. The dielectric features of the $BaTiO_3$ are significant in microelectronic devices production. $BaTiO_3$ nano and microstructures with high purity are essential for the production of these microelectronics [1].

There are many methods for the synthesis of barium titanate system in the literature. The solid-state method, co-precipitation, sol-gel process and hydrothermal synthesis can be used to synthesize Barium titanate perovskite structures [2-6]. Considering these methods in general, there are disadvantages such as high temperature when using metal oxides and derivatives in the solid-state method, the use of expensive and air-sensitive starting materials in some other techniques (use of air-sensitive $TiCl_4$, etc.), inhomogeneous distribution, porous structure. Recently, researchers have focused on new methods of synthesis (sonochemical, flame spray pyrolysis) at low temperatures in various sizes and morphology. However, these new methods are generally costly compared to existing powder production techniques [7-9].

To address the above problems, wet chemical methods have been systematically studied to synthesize high-quality ceramic materials. In particular, the Pechini method (Polymeric precursor technique) has advantages over other chemical processes such as controlling stoichiometry, lower reaction temperature, higher

chemical homogeneity, and distribution equation, obtaining nanoscale particles and smaller grain size [6, 10, 11].

In the Pechini process, metals form a complex with citric acid in the aqueous solution. Ethylene glycol, which is a polyalcohol-like, is added to this solution and heated at high temperatures. The gel is obtained as a result of the polyesterification of metal chelates. It is possible to obtain nano-sized crystallites by thermal decomposition of the gel. A large number of mixed oxide compositions can be prepared using this method [12, 13].

In the present study, the Pechini synthesis procedure was utilized to sufficiently prepare $BaTiO_3$ nanostructures. The obtained results pointed out that this technique is a promising option for good chemical homogeneity and precise control of the stoichiometry. The study also aims to produce high-quality materials at an industrial scale and economy by consuming commercially available organic titanate.

2. Materials and Methods

Barium acetate ($Ba(CH_3COO)_2$, 99% purity, Sigma-Aldrich), titanium(triethanolaminato) isopropoxide solution (80%wt. in isopropanol, Sigma Aldrich), citric acid ($C_6H_8O_7$,≥ 99.5%, Sigma-Aldrich) and ethylene glycol ($C_2H_6O_2$, 99.8%, Sigma-Aldrich) were used as starting materials. FTIR spectra of the samples were recorded on Spectrum BX Perkin Elmer FT-IR System spectrometer using KBr pellets. Thermogravimetric analysis was performed with an SII 7300 Perkin Elmer thermal analyzer using flowing N_2 at 2.5 mL/min from 25 to 1200°C at a heating rate of 10°C/min. The powders were characterized by using X-ray diffraction (XRD) on a PANalytical Empyrean diffractometer with Cu K_α radiation (λ= 1.5406Å). Match! Version 3 Crystal impact was used for phase identification [14]. The X-ray pattern of the corresponding compound was analyzed by Rietveld refinement program FULLPROF [15]. The crystallite size estimation calculation for the corresponding phase was done by using the Scherrer formula:

$$L \text{ (average in Å)} = K\lambda / (FWHM{*}cos\theta)$$

where L refers to crystallite size, K is the Scherrer constant, λ is the wavelength of the radiation, θ is the diffraction angle of the peak, and $FWHM$ is the full width at half maximum of (110) peak. Scanning electron microscopy (SEM) was used to analyze the morphology of the $BaTiO_3$ structure. SEM images were taken by a Zeiss Gemini 500 microscope. The average particle diameters were measured from each SEM image. Energy-dispersive X-ray spectroscope (EDX) was used to ascertain the chemical composition of the material.

2.1. Preparation of $BaTiO_3$ nanoparticles

The $BaTiO_3$ nanoparticles were prepared by the Pechini technique. The flow chart of the method is given in Figure 1. The metal-citrate solutions were prepared using barium acetate, titanium(IV) (triethanolaminato) isopropoxide, citric acid and ethylene glycol. Considering the molar amounts of starting precursors, molar ratio can be expressed as $Ba(CH_3COO)_2$: organic titanate: citric acid: ethylene glycol = 1: 1: 4.5: 20.
The preparation steps are given below.

Preparation of Barium Citrate Solution
2.02 g (7.90 mmol) of barium acetate was dissolved in ~2.7 mL ethylene glycol, and 1.51 g citric acid was then added to this solution.

Preparation of Titanium Citrate Solution
Titanium citrate solution was prepared by mixing 2.5 g (7.90 mmol) titanium (triethanolaminato)isopropoxide (80% wt. in isopropanol) and 5.31 g citric acid in 6.2 mL ethylene glycol.

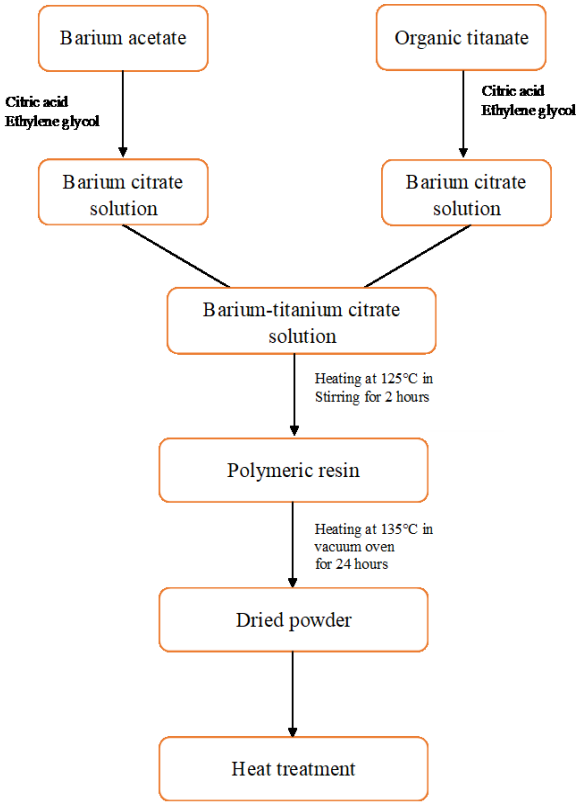

Figure 1. Flow chart of the synthesis of $BaTiO_3$ using the Pechini method.

Finally, two solutions (barium citrate and titanium citrate) were mixed, and a clear yellow solution was achieved. After stirring at 125°C for 2 hours, the yellow gel was obtained. The polymeric gel was heated in a vacuum oven at 135°C for 24 hours to obtain a dry powder. The dried powder was heated up in two steps:

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firstly, at 400°C for 4 hours, then treated at 800ºC for 4 hours with a heating rate of 10ºC/min and then slowly cooled at room temperature.

The minor amount of $BaCO_3$ was typically observed, which result in regards to the open-air system. Powder samples were washed with acetic to remove the undesired $BaCO_3$ phase.

3. Results and Discussion

3.1. X-ray diffraction and Rietveld Refinement

The XRD pattern of the heat-treated at 800°C $BaTiO_3$ powder synthesized via the Pechini method is presented in Figure 2. The XRD and Rietveld refinement results obtained from in this study positively confirmed the $BaTiO_3$ phase maintains a cubic crystal system. The refinements of the crystal structure were performed by the Rietveld method. Rietveld refinement results of XRD profiles are given in Figure 3. All the peaks are indexed (identified using JCPDS:79-2263) for cubic phase formation, and lattice powders indicate the formation of the cubic phase, which belongs to space group *Pm-3m* (#221). The lattice parameters obtained from Rietveld refinement were a=4.0047Å, V=64.22 Å^{3,} and the calculated density is found 6.03 g/cm^3. The parameters of refinement are R_F= 2.89 and χ^2= 3.56. The reliability factors and refined structural parameters of $BaTiO_3$ are summarized in Table 1. In table 1, R factors present a good agreement between refined and experimental XRD profile for barium titanate. The average crystallite sizes, as estimated by Scherrer formula was 51.9 nm for calcined temperature 800ºC using (110) major diffraction peak.

Table 1. Structure refinement parameters and crystal data for $BaTiO_3$.

Formula	$BaTiO_3$
Formula weight	233.13 g/mol
Temperature (K)	298
λ (Å)	1.54060
Crystal system	cubic
space group	*Pm-3m* (#221)
Unit cell dimensions	a=4.0047Å,
V (Å^3)	64.22
Calc. Density (g/cm^3)	6.03
2θ range	10.0078-79.9922
(step)(°)	0.0131
$\chi 2$	3.56
R_F ,R_{Bragg}(%)	2.89, 4.48
R_p, R_{wp}, R_{exp} (%)	13.3, 11.4, 6.02

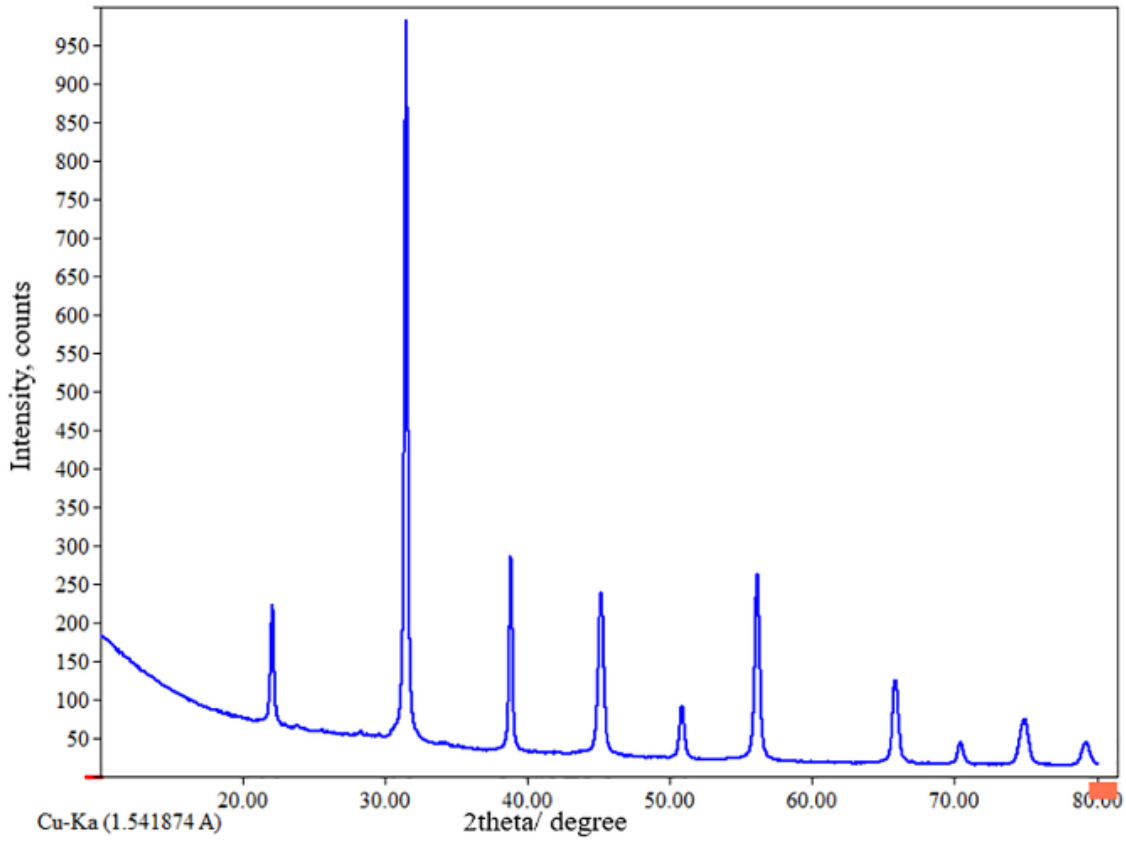

Figure 2. XRD pattern of $BaTiO_3$ nanopowders calcined for 4 hours at 800 ºC.

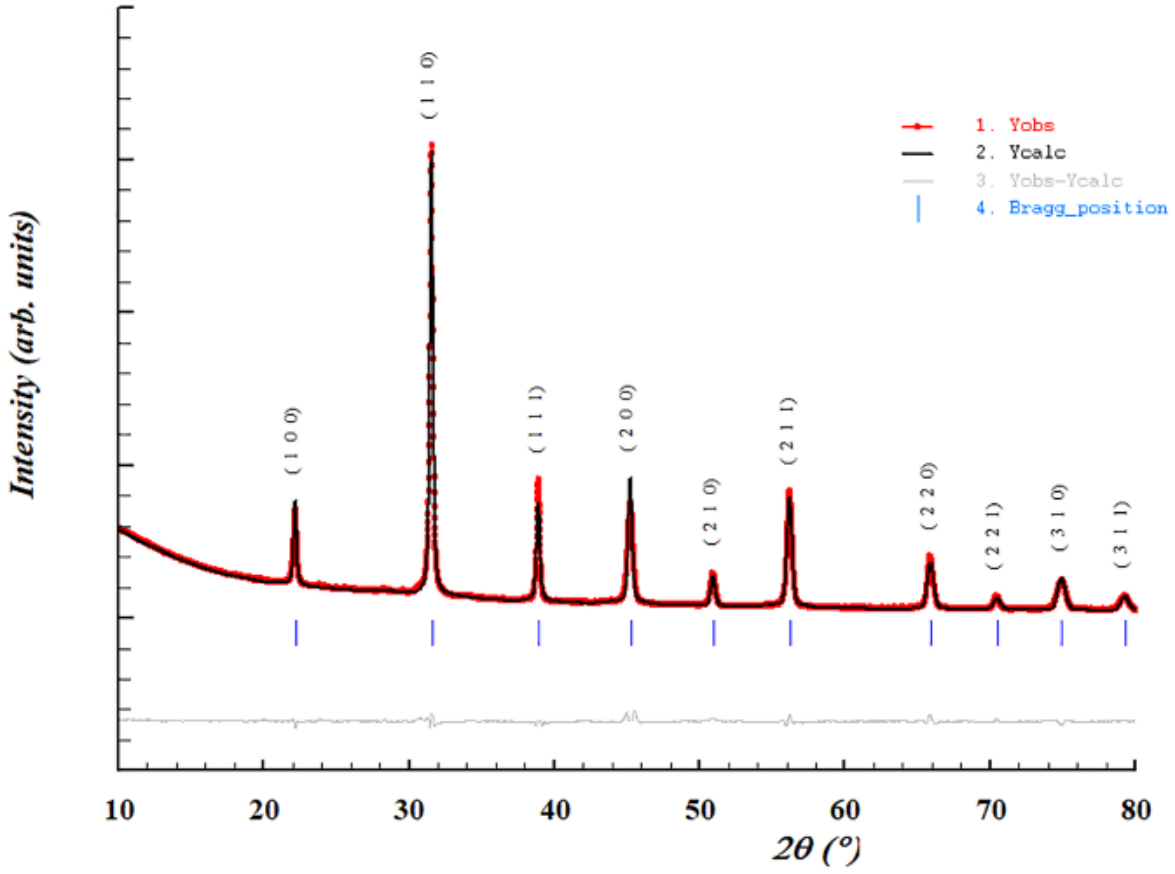

Figure 3. Rietveld refinement of $BaTiO_3$ calcined at 800 ºC for 4 hours. Experimental (1) and calculated (2) diffraction patterns of $BaTiO_3$ after Rietveld refinement. Difference (3), Bragg Positions (4).

The crystal structure of $BaTiO_3$ is shown in Figure 4. Ba^{2+} traditionally builds a cuboid box, and TiO_6 octahedron falls within the box. Ti^{4+} is ideally placed around the center of the oxygen octahedron. It can be recognized that Barium atom has 12-fold coordination for Ti atom is 6. The crystal structure was pictured by the VESTA program [16].

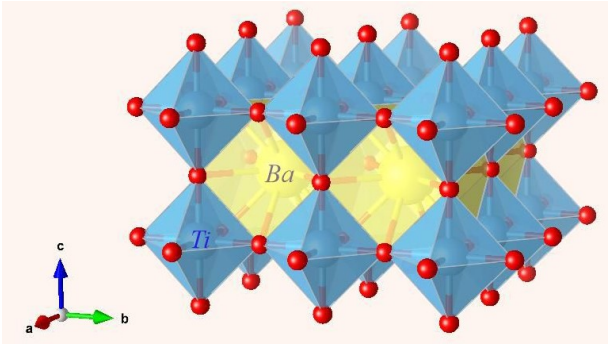

Figure 4. Schematic illustration of the refined crystal structure of the Barium titanate. Ba: yellow, Ti: blue, O: red colored.

3.2. Thermal Analysis

The thermal analysis of the $BaTiO_3$ synthesized through the Pechini method was carried out using DTG, DTA, and TGA up to 1200 °C at a heating rate of 10°C/min. Figure 5. indicated the TGA, DTA, and DTG plots of the as-prepared powders of $BaTiO_3$. The thermal analysis of Barium titanate shows two degradations. The first weight loss for a temperature range between 25°C and 200°C in the TGA curve is 5% and which corresponds to the adsorbed moisture and volatiles present in the sample. This weight loss indicated a maximum at 160°C in the DTG curve. The second weight loss between 200-600°C is due to dehydration and destruction of organic molecules, which are also observed at the FT-IR spectrum of dried powder at 135°C. Finally, between 630 and 850°C, the powder weight remains almost stable, with a total reduction of 1% may be due to the evolution of CO_2 and CO. After the calcination process at 800°C, 25% of powder was obtained, as seen in the TGA profile.

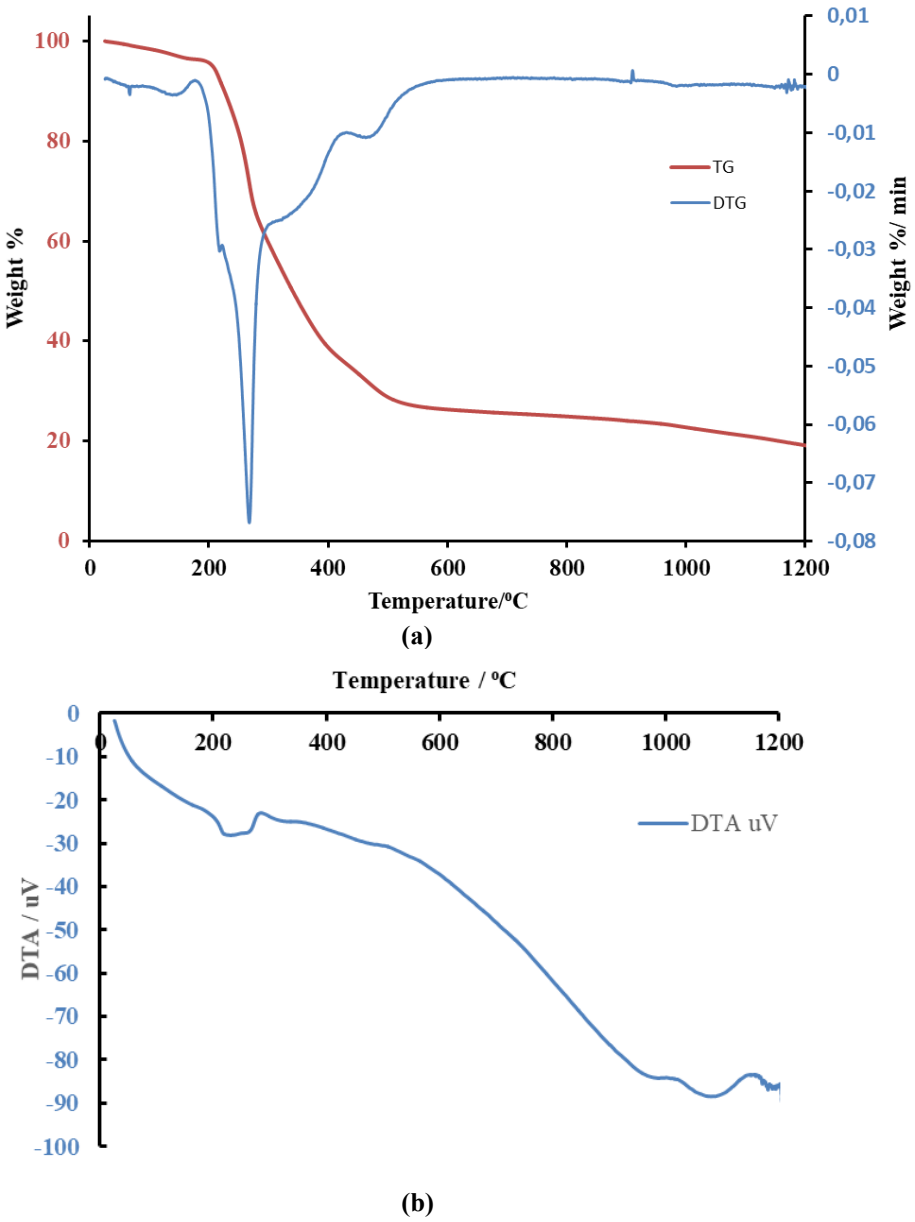

Figure 5. TGA, DTG (a) and DTA (b) plots of as-prepared $BaTiO_3$ powder.

3.3. FT-IR Analysis

In order to understand the thermal decomposition of the organic components in the reaction medium, FT-IR analysis was achieved. The spectrum of the gel powder (at 135°C) shows bands at 3319, 2958, 1739, 1591, 1181, 1076, 647, and 543 cm^{-1}. The absorption bands at 3319, 2958 cm^{-1} are assigned to O-H and C-H stretching vibrations, respectively, as well as confirm absorbed moisture and presence of $–CH_2$ and $–CH_3$ organic groups. Two peaks at 1739 and 1591 cm^{-1} indicate the existence of acetate groups also supports the symmetric and asymmetric stretching vibrations of carboxylate [17]. When the temperature reaches 400°C, a significant change is observed in the IR spectrum. The bands of organic groups have disappeared. Two new peaks in 1441 and 858 cm^{-1} indicate the presence of $BaCO_3$. After calcination at 800°C, these peaks are disappeared. The new bands below 800 cm^{-1} indicate the formation of the $BaTiO_3$ structure. The FTIR spectrum of $BaTiO_3$ has characteristic absorption peaks between 800–400 cm^{-1}, related to used to identify the phase formation [18]. A new broad absorption peak at 576 cm^{-1} is due to the stretching vibration of Ti-O. These FT-IR analysis results confirm the formation of the $BaTiO_3$ structure.

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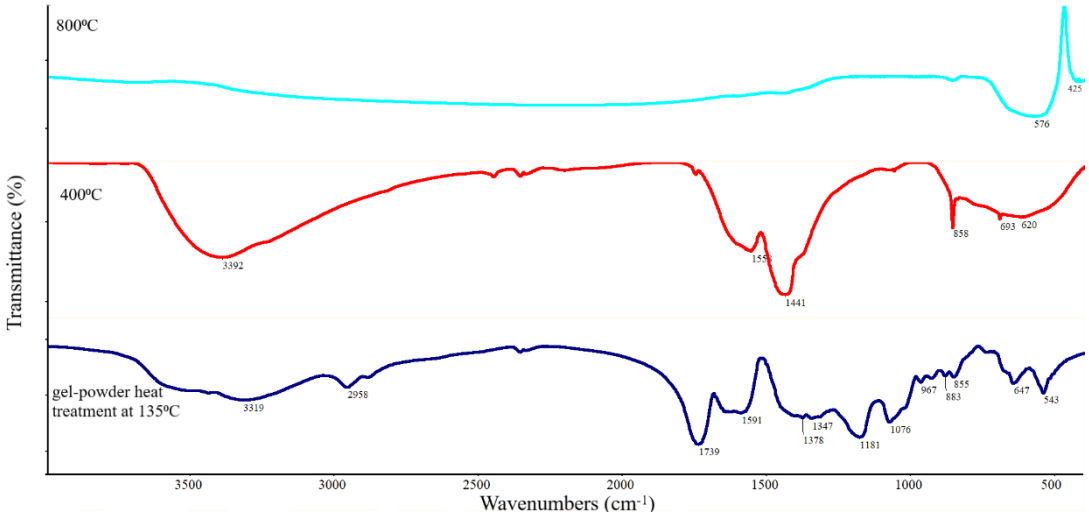
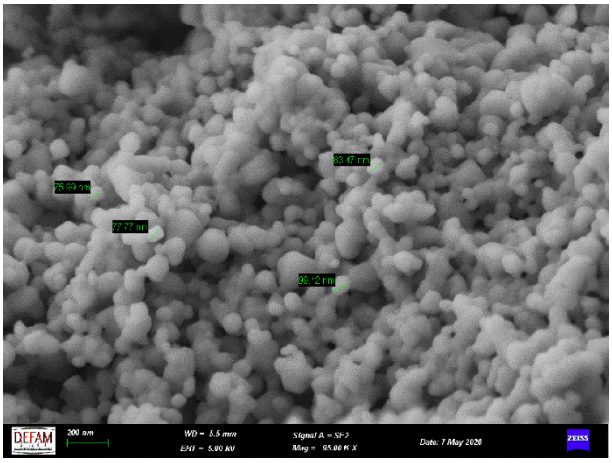


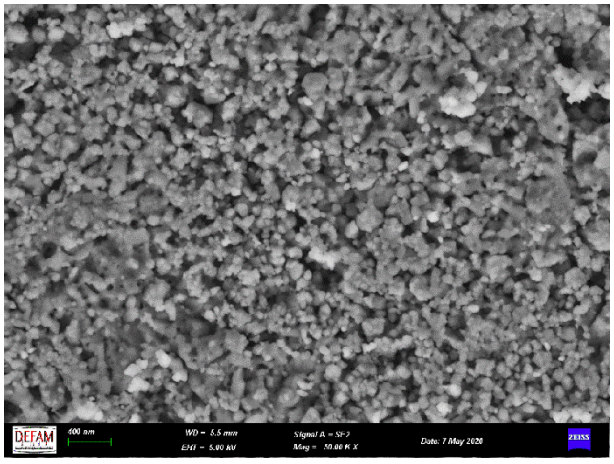
Figure 6. FT-IR spectra of $BaTiO_3$ samples at different temperatures.

3.4. SEM and EDX Analysis

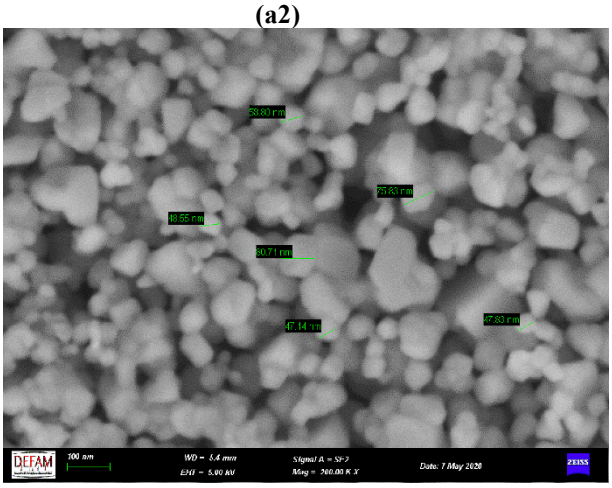
The surface morphology of the calcined sample of $BaTiO_3$ was investigated by scanning electron microscopy, which is presented in Figure 7. Figure 7(a1) shows particles and their agglomerates. The powders have been agglomerated because of various operations during the heat treatment of the gel precursor. There are small and spherical particles coalesced in each cluster. As shown in Figure (a2 and a3), round-shaped grains were observed with an approximate diameter of 40-90 nm.
EDX analysis of particles calcined at 800°C is given in Figure 8 and confirmed the accuracy of elemental composition. The particles are composed of Ba, Ti, and O elements.



(a2)



(a1)



(a3)

Figure 7. SEM images of $BaTiO_3$ samples synthesized at 800ºC by Pechini process (a1) 50.000 zoom, (a2) 95.000 zoom, (a3) 200.000 zoom. Detected grain sizes from selected points (a2: 75.99, 77.77, 99.12, 83.47 nm; a3: 47.14, 47.83, 48.55, 58.80, 75.83, 80.71 nm).

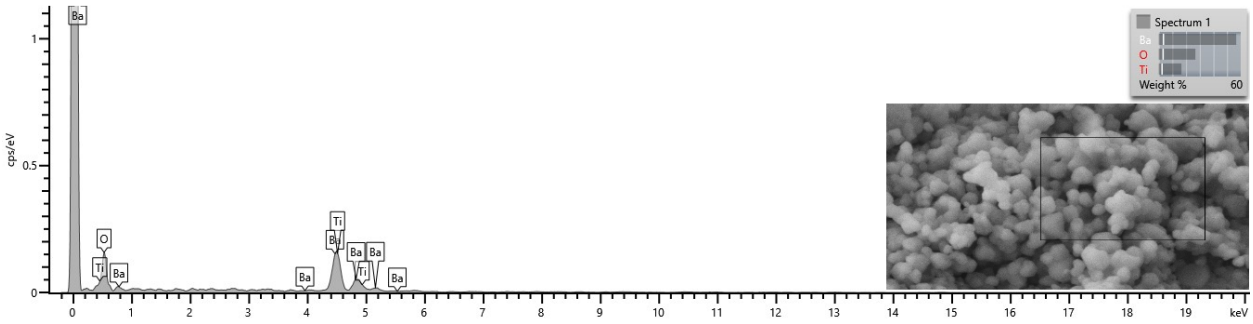


Figure 8. EDX analysis of particles calcined at 800ºC.

Table 1. Experimental conditions for $BaTiO_3$ by Pechini and Sol-precipitation method.

Method	Precursors	Conditions	Phase	Morphologies (Grain size)	Reference
Pechini	$Ba(CH_3COO)_2$ organic titanate	4h, 800°C	Cubic	40-90 nm	In the present study
Pechini	$Ba(CH_3COO)_2$ Ti-isopropoxide	5h, 600°C	Cubic	44±15 nm	[5]
Pechini	$Ba(CH_3COO)_2$ Ti-isopropoxide	3 h, 700ºC	Pseudo-cubic	40-80 nm	[19]
Pechini	$Ba(CH_3COO)_2$ Tetra butyl titanate	6h, 720°C	Cubic	20-130 nm	[20]
Sol-precipitation	$Ba(OH)_2$ organic titanate	12h, 400°C	Cubic	23-31 nm	[4]

*organic titanate: titanium(IV)(triethanolaminato)isopropoxide

3.5. Comparison of results with literature data

The synthesis processes of $BaTiO_3$ are summarized in Table I (also include the corresponding literature for comparison). In the present study, $BaTiO_3$ was synthesized from $Ba(CH_3COO)_2$ and organic titanate precursor with 40-90 nm grain size. When compared with the reactions performed with the Pechini method using Barium acetate, it is seen that the obtained barium titanate is in the cubic phase and has similar morphological properties. In these methods, an expensive and easily hydrolyzable titanium precursor is used. The Pechini method is more advantageous than the conditions realized using organic titanate with the sol-precipitation [4] method. The smaller grain size was obtained by stirring at high speed, precipitated with the centrifuge, and sintering for 12 hours. The industrial application of the method is not beneficial. In the present study, the synthesis process was demonstrated favorable properties, such as lack of a minor second phase, using economically inexpensive non-air sensitive precursors, simply applicability in the industry.

4. Conclusion

In this paper, nanoscale barium titanate powders have been synthesized from gel precursors by the Pechini process. In the process, it is advantageous to use titanium (triethanolaminato)isopropoxide, which is not sensitive to air and cheap as a starting material. The XRD results of the $BaTiO_3$ sample indicated that the material is in pure phase with a cubic structure. TGA-DTG and FT-IR analyses confirm that the nanopowders were obtained at a calcination temperature of 800°C. The average crystallite size was 51.8 nm, as determined by XRD. SEM analyses were showed that the grains were agglomerated, and the grain size determined between 40-90 nm.

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Author's Contributions

Pelin Sözen Aktaş: Performed the experiments, analyzed the results and wrote the manuscript.

Ethics

There are no ethical issues after the publication of this manuscript.

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