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Effect of powder synthesis method on $BaTiO_3$ ceramics

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Abstract

Barium titanate ($BaTiO_3$) has been of practical interest for more than 60 years because of its attractive properties. $BaTiO_3$ can be prepared using different methods, which can have significant influence on the structure and properties of barium titanate ceramics.

In this paper powder of $BaTiO_3$ powders were prepared by two methods. The first was synthesis from polymeric precursors through Pechini process which was carried out as a three-stage process from an oganometallic complex, producing cubic $BaTiO_3$ powders with 40–80 nm primary particles. The second was a mechanochemical synthesis from powder mixture of BaO and TiO_2, producing cubic $BaTiO_3$ but with primary particles 200–250 nm. In both cases $BaTiO_3$ ceramics were produced by sintering for 2h at 1300°C without a pre-calcination step. The phases formed and the crystal structure of $BaTiO_3$ prepared by both methods was carried out by XRD analysis. The morphology and microstructure of obtained powders and sintered samples were examined by SEM.

Keywords: barium titanate, synthesis, microstructures

I. Introduction

Barium titanate ($BaTiO_3$) has been of practical interest for more than 60 years because of its attractive properties. Firstly, because it is chemically and mechanically very stable, secondly, because it exhibits ferroelectric properties at and above room temperature, and finally because it can be easily prepared and used in the form of ceramic polycrystalline samples. Barium titanate is the first discovered ferroelectric perovskite. Due to its high dielectric constant and low dielectric loss characteristics barium titanate ($BaTiO_3$) has been used in applications such as capacitors and multilayer capacitors (MLC-s) and energy storage devices. There is existing demand for fabrication of fine particle, nanosized powders <100 nm to allow the production of thinner layers for MLC-s and cheaper or more reliable routes than current practice.

Chemical synthesis of barium titanate has developed through techniques such as sol-gel, coprecipitation, hydrothermal and polymeric precursor methods [1]. The advantage of chemical methods is the quasi-atomic dispersion of constituent components in liquid precursor, which facilitates synthesis of crystallized powder with submicron particles and high purity at low temperatures. The advantage of the Pechini method or polymeric precursors method (PPM) is based on the fact of its simplicity and possibility to maintain the initial stoichiometry of the starting solution.

An alternative method to chemical synthesis is mechanochemical synthesis by ball milling. The mechanical activation is very effective method for obtaining highly dispersed system due to mechanical action stress fields formed in solids during milling procedure [2]. Under the high energy milling conditions, there is release of heat, formation of new surfaces, formations of different crystal lattice defects and initiation of solid-state reaction. The accumulated deformation energy is the key to

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understanding the route of irreversible changes of crystal structure and consequently microstructure causing the change of properties of $BaTiO_3$ produced using this method [3,4]. In this paper, we used two methods for synthesis of $BaTiO_3$ powder, PPM and mechanochemical method, to investigate the influence of the synthesis method on $BaTiO_3$ structure and properties.

II. Experimental

Barium titanate ($BaTiO_3$) powder was prepared by the polymeric organometallic precursors method (Pechini process-PPM) using barium and titanium citrates. Titanium citrate solution was prepared by dissolving titanium-tetra-isopropoxide $Ti[OCH(CH_3)_2]_4$ (Alfa Aesar, 99.995%) in ethylene glycol ($HOCH_2CH_2OH$). This solution was heated at T>60°C with constant stirring for 10 min. Afterwards, the citric acid (Carlo Erba, 99.8%) was added. The solution of titanium citrate was mixed and heated at 90°C. Simultaneously, barium citrate solution was prepared by dissolving barium acetate (Alfa Aesar, 99.0–102.0%) in citric acid solution. This solution was heated at 90°C and when transparent, ethylene glycol was added. The molar ratio of citric acid to ethylene glycol was 1 : 4, for both citrate solutions. Solutions of titanium citrate and barium citrate were mixed, with constant stirring until it became clear transparent yellow solution. Temperature was raised up to 120–140°C, to promote polymerization and remove solvents. Solution became more viscous and colour changes from yellow to brown and finally solution solidifies into a dark-brown glassy resin [5]. Decomposition of most of the organic C residue was performed in an oven at 250°C for 1h and then at 300°C for 4h, the heating rate was 2 °C/min. The resin became a black solid mass and material was pulverized, using Agate Mortar and pestle, before further treatment. Thermal treatment was performed at 500°C for 4h, 700°C for 3h and 750°C for 2h. The agglomerates were broken in agate pulverizer (Fritisch Pulverisette, Type 02.102). After drying at room temperature and passing through sieve (200 mesh), the barium titanate powder was obtained [6]. The flow chart for the PPM is shown in Fig. 1.

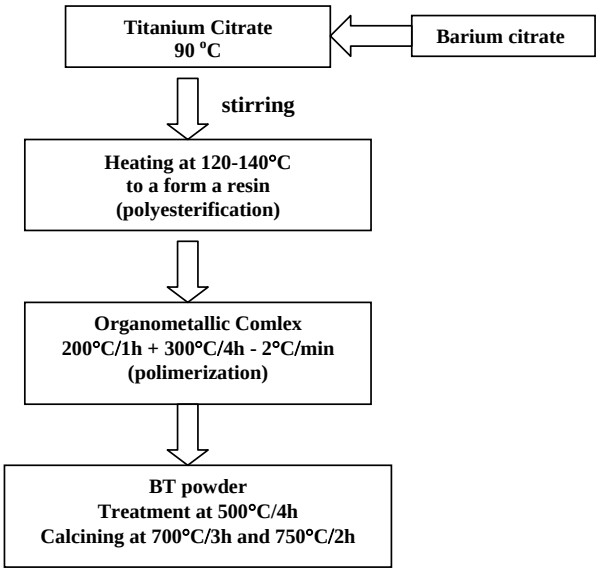


Figure 1. The flow chart for the Pechini process

$BaTiO_3$ was also prepared by mechanochemical synthesis starting from barium oxide (BaO, Alfa Aesar, 88%, $d < 100$ nm) and titanium oxide in the anatase crystal form (TiO_2, Reagelte Ruro Carlo Erba, 99%, $d \sim 35$ nm). A equimolar mixture of BaO and TiO_2 was treated in a planetary ball mill (Fritsch Pulverisette 2). The milling medium used was zirconium oxide balls around 10 mm in diameter. Zirconium oxide vial of 500 cm^3 was used. Mass of the mixture was 25 g per a vial. The mass ratio, ball to powder was 20 : 1. The angular velocity of the supporting disk and vials was 38.04 rad/s (363 rpm). Milling time was 1h [7].

The powders synthesized with both methods were pressed at 98.1 MPa, into 8 × 2.5 mm^2 pallets, using a cold isostatic press. The samples were sintered at 1300°C for 2h (in the tube furnace "Lenton", UK). The heating rate was 10 °C/min, with natural cooling in an air atmosphere.

III. Characterization

The X-ray diffraction (XRD) data for barium titanate powders and for sintered samples were measured using CuKα radiation and a graphite monochromator (Model Phillips PW1710 difractometer) under the following experimental conditions: 40 KV, 2θ=10–120°, with a step size of 0.020°. Specific surface areas (*SS* were measured by nitrogen adsorption (Gemini 2375, Micromeritics) and average particle diameters (D_{BET}) were calculated from the *SSA* ($6/\rho \cdot SSA$). Density of barium titanate ceramics was obtained by measuring dimensions of the samples and calculating from equation $\rho = 4 \cdot m/d^2 \cdot h \cdot \pi$ (where m is mass, d - average diameter and h - height of the sintered samples).

The grain sizes and morphology were examined using a scanning electron microscope (Model JEOL – JSM 5300). The microstructure of sintered samples was obtained by polishing and some of the samples were chemically etched by the mixture of 10% HCl with 5% HF for 60 s.

IV. Results and Discussion

The XRD results of powders from both synthesis routes (Fig. 2) indicate the formation of the cubic phase of $BaTiO_3$ (identified using the JCPDS files no. 31-0174). It can be observed that in the case of PPM, $BaTiO_3$ powder is well crystallized but in the case of mechanochemistry process, significant amount of amorphous phase was detected. However, the XRD results of sintered samples prepared by both methods (Fig. 3) show the formation

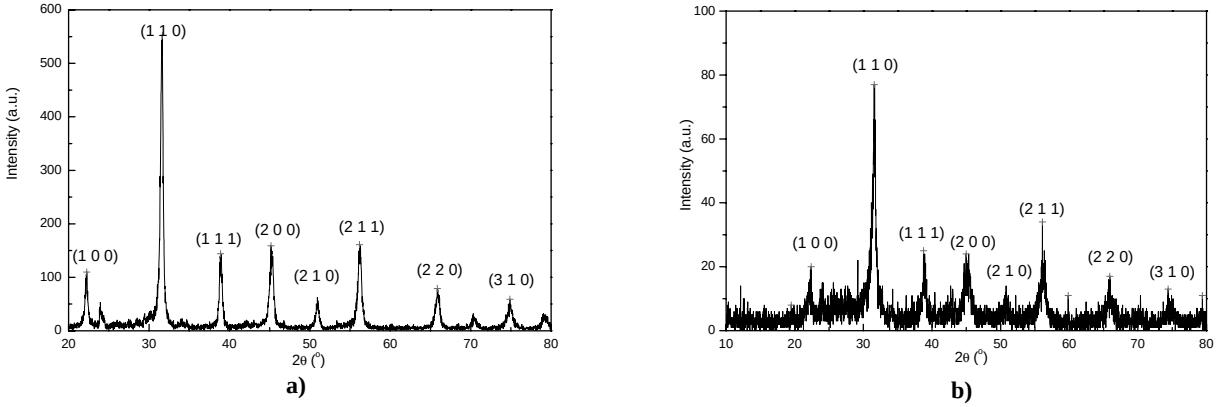


Figure 2. X-ray diffraction of $BaTiO_3$ powder prepared by: a) Pechini method and b) mechanochemical method

of well crystallized tetragonal phase of $BaTiO_3$ (identified using the JCPDS files no. 05-0626). Tetragonality turns out to be very low c/a = 1.005 and 1.009 for PPM and mechanochemical method, respectively [8]. Density of samples sintered at 1300°C for 2h was about 91% of theoretical density for PPM and about 82% for samples obtained by other method.

Fig. 4 shows the SEM photographs of the $BaTiO_3$ synthesized by PPM (Fig. 4a) and mechanochemically (Fig. 4b). The morphology of the powders indicates the presence of individual particles and its agglomerates. The dimensions of agglomerates and particles depend on the synthesis method. The powder prepared mechanochemically possesses higher number of agglomerates, the particles are bigger and with irregular shape in the comparison that powder obtained by PPM where primary particles are spherical. The primary particle size is approximately 40–80 nm and 200–250 nm for the PPM and mechanochemical process, respectively.

The specific surface area of $BaTiO_3$ powders prepared by PPM was about 13.47 m^2/g and for other method 4.42 m^2/g. The calculated equivalent particle size from the expression $D = 6/\rho \cdot SSA$, (D is average diameter of spherical particles, SSA the surface area of obtained powders and ρ the theoretical density of $BaTiO_3$) for PPM and mechanochemical method was about 70 nm and 225 nm, respectively. Those results are in agreement with results obtained by SEM.

The microstructure observed at free surface of samples sintered at 1300°C for 2 hours for both type of powder synthesis is given on Fig. 5. The average grain size of sintered sample prepared by PPM is around 400 nm, grains have rounded shape and approximately same dimensions indicating the homogeneous microstructure. In the case of BT prepared from powders obtained by mechanochemical synthesis, the grains are much bigger, around 0.75–4 μm with polygonal shape. The obtained microstructure indicates that chemical method for powder preparation leads to homogeneous microstructure with small grains comparing to other method that leads to inhomogeneous microstructure with irregular grains.

Obtained microstructures indicate that the PPM route is seen to be more suitable for the production of nanosized powders and fine grained ceramics. From our qualitative estimation of the powder primary particles (40–80 nm) and sintered grain size (400 nm) there is however a grain growth factor of about 10. In the case of the powder prepared by mechanochemical synthesis (primary particles around 200–250 nm and sintered grains size about 0.75–4 μm) grain growth factor is from 5–16. This high grain growth factor is probably associated with a degree of agglomeration of the $BaTiO_3$ powder.

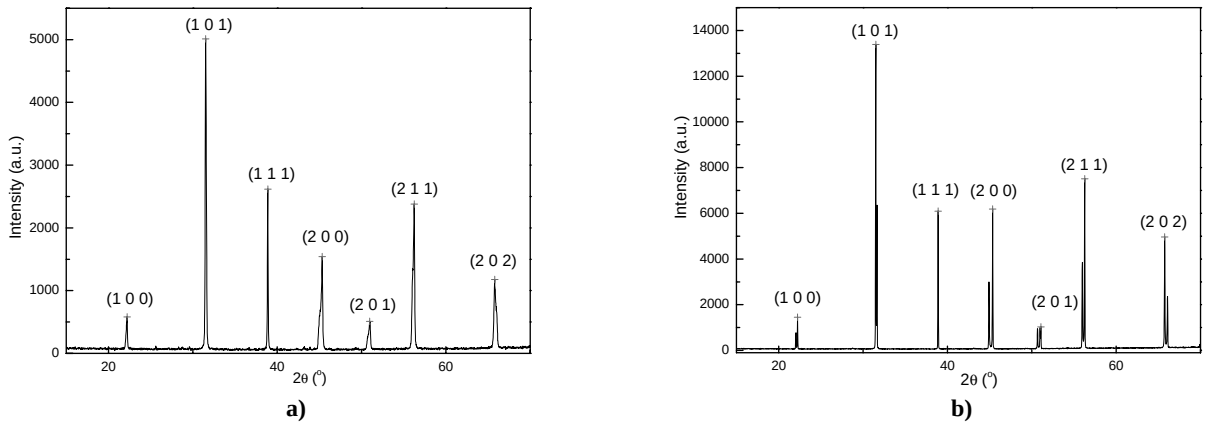
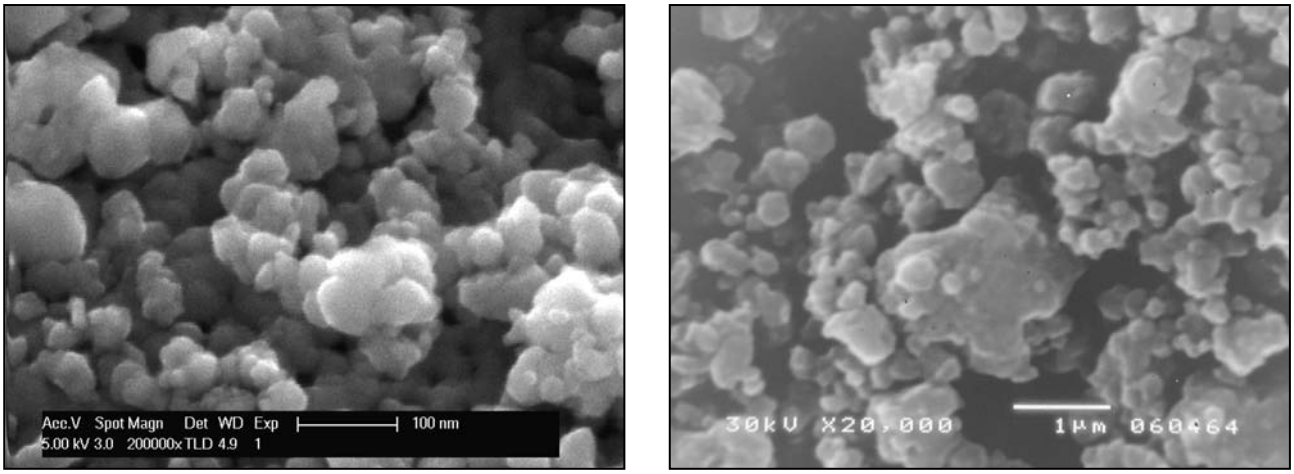
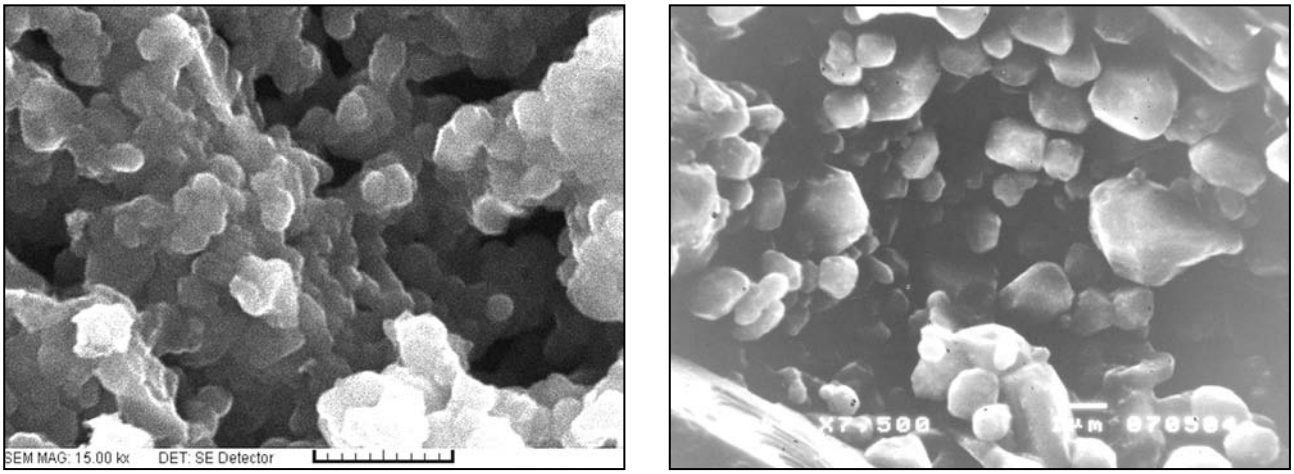


Figure 3. X-ray diffraction of $BaTiO_3$ sintered sample prepared by: a) Pechini method and b) mechanochemical method



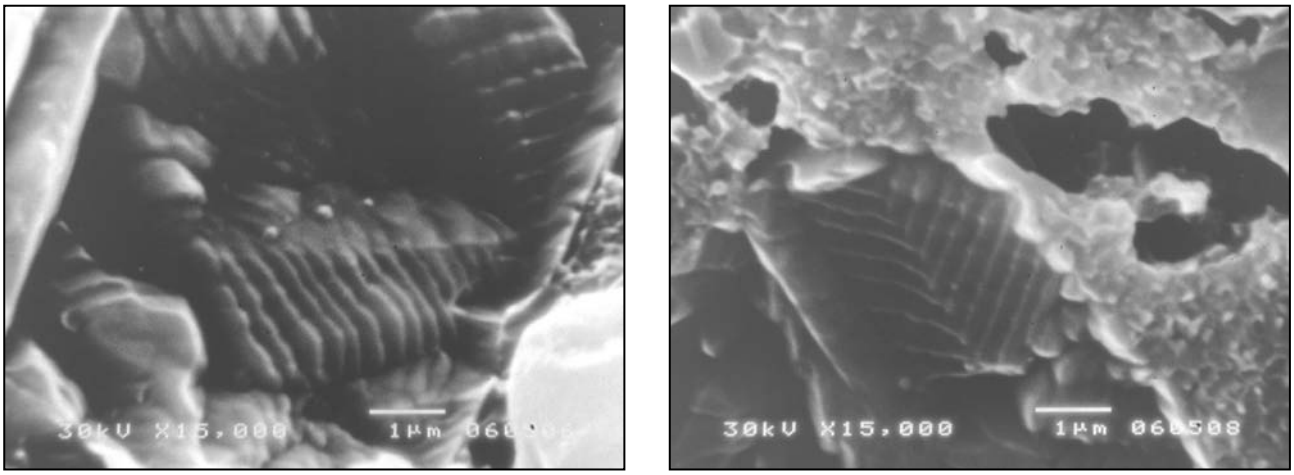
a) **b)**

Figure 4. Microstructure of $BaTiO_3$ powders:
(a) synthesized by Pechini process and
(b) synthesized mechanochemically



a) **b)**

Figure 5. Microstructure of $BaTiO_3$ sintered samples:
(a) synthesized by Pechini process and
(b) synthesized mechanochemically



a) **b)**

Figure 6. SEM micrograph of domain structure in $BaTiO_3$ sample sintered at 1300°C for 2h and prepared by Pechini process

Future work is planned to both characterize with more quantitatively the degree of agglomeration and to try and reduce it by adding a milling step between the final thermal treatment and the isostatic pressing for PPM route. To reduce number of agglomerates of $BaTiO_3$ obtained by mechanochemical synthesis, ultrasonic horn method could be very effective method for deagglomeration [9].

These proposed approaches should allow us to further assess the promise of the PPM and mechanochemical route for nanosized $BaTiO_3$ powder synthesis.

It is known that in fine-grained materials with grain size of about 1 μm, the domains are only visible at SEM after chemical etching [10]. Fig. 6 represents the SEM photographs of $BaTiO_3$ prepared by PPM, sintered at 1300°C for 2h and etched in 10% HCl with 5% HF for 60 s. It was observed two types of domain configuration. The fine parallel lines were identified as 90° walls (Fig. 6a) and the herringbone pattern (Fig. 6b) which is described as 180° walls separating the regions with different polarization [11]. The wall thickness ranges from 0.08 μm up to 0.14 μm and from 0.14 μm up to 0.17 μm for 90° and 180° domains, respectively. The domain width is around 0.20 μm for both types of domains.

V. Conclusions

It has been demonstrated that pure $BaTiO_3$ can be successfully prepared by two methods, polymeric organometallic precursors process and mechanochemically. The XRD results of powders obtained by both methods indicate the formation of cubic phase of $BaTiO_3$ and tetragonal phase in sintered samples. The $BaTiO_3$ powder prepared by PPM was well crystallized but a significant amount of amorphous phase was detected for the mechanochemical method. The influence of the powder synthesis method on the resulting sintered microstructure was analyzed. Two types of domain configuration, 90° and 180° domains were observed in chemically etched sintered samples, prepared from powders obtained by PPM process.

The PPM route produced primary particles of around 40–80 nm and despite heavy agglomeration sintered well at 1300°C to produce fine sub-micron ceramics with controlled stoichiometry. The PPM route thus has promise for the production of nanosized $BaTiO_3$ powders small batches if the degree of agglomeration can be reduced.

Mechanochemical synthesis of ceramic powders also can make possible to obtain nanostructured powders. Due to low energy costs and rapid synthesis this method can be very useful for industrial production of nanosized powders.

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