The characterization of the barium titanate ceramic powders prepared by the Pechini type reaction route and mechanically assisted synthesis

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Available online 4 September 2009

Abstract

$BaTiO_3$ ceramic powders were prepared by a complex method based on the Pechini type reaction route and mechanically assisted synthesis. In both ways $BaTiO_3$ ceramics were sintered after 120 min on 1300 °C without pre-calcination steps. The crystal structure was investigated by the XRD, IR and Raman spectroscopy. The particle size and morphology of $BaTiO_3$ were examined by XRD and SEM. The XRD results of powders indicate the formation of cubic phase of $BaTiO_3$. It can be observed that in the case of Pechini process $BaTiO_3$ powder is well crystallized but in the case of mechanochemistry process, significant amount of amorphous phase was detected. The sintered $BaTiO_3$ ceramic sample prepared by Pechini process, shows the formation of tetragonal phase. However, IR and Raman spectrum showed a mixture of cubic and tetragonal for $BaTiO_3$ obtained by Pechini process and tetragonal for $BaTiO_3$ obtained by mechanically assisted synthesis.
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Keywords: Calcination; Sintering; Spectroscopy; X-ray methods

1. Introduction

Barium titanate ($BaTiO_3$, BT) belongs to the family of the perovskite-type (ABO_3) structure. $BaTiO_3$ powders are widely utilized to manufacture electronic components such as multilayer ceramic capacitors (MLCs),[1,2] PTC thermistors,[3] piezoelectric transducers[4] and a variety of electro-optic devices,[1,5] due to its high dielectric constant[6] and good ferro-electric properties.[7]

Chemical synthesis has grown up through techniques of sol–gel, coprecipitation, hydrothermal and polymeric precursor method.[8] The advantage of chemical methods is the quasi-atomic dispersion of constituent components in liquid precursor, which facilitates synthesis of crystallized powder with sub-micron particles and high purity at low temperatures. The advantage of Pechini method (polymeric precursor method) is based on the fact of its simplicity and possibility to hold the initial stoichiometry.[9]

The mechanical activation is very effective method for obtaining highly dispersed system due to mechanical action stress fields formed in solids during milling procedure.[10] Under conditions of milling, the releasing of heat, formation of new surfaces, formations of different crystal lattice defects and initiation of solid-state reaction are found. The accumulated deformation energy is the key of understanding the route of irreversible changes of crystal structure and consequently microstructure, causing in the change of properties of our material.[11] In this paper, we used two methods for synthesis of $BaTiO_3$ powder, Pechini process and mechanochemical method. It was to investigate the influence of method of powder synthesis on $BaTiO_3$ structure and properties.

2. Experimental procedure

Barium titanate ($BaTiO_3$) powder was prepared by the polymeric organometallic precursors method (Pechini process) 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 solution of citric acid (Carlo Erba, 99.8 %) was added very slowly. 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 with constant stirring until it became clear transparent yellow solution. The molar ratio of citric acid to ethylene glycol was 1:4. 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 color changes from yellow to brown and finally solution solidifies into a dark-brown glassy resin.[9] Decomposition of most of the organic C residue was performed in an oven at 250 °C for 1 h and then at 300 °C for 4 h, the heating rate was 2 °C min^{-1}. The resin became a block solid mass and material was pulverized, using Agate Mortar and pestle, before further treatment. Thermal treatment was performed at 500 °C for 4 h, 700 °C for 3 h and 750 °C for 2 h. The agglomerates were broken in agate pulverize (Fritsch Pulverisette, Type 02.102). After drying at room temperature and passing through sieve (200 meshes), the barium titanate powder was obtained.[12]

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). An 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 diameters. Zirconium oxide vial of 500 cm^3 was used. Mass of the mixture was 25 g per vial. The mass ratio ball to powder was 20:1. The angular velocity of the supporting disk and vials was 38.04 rad s^{-1} (363 rpm). Milling time was 1 h.

The powders synthesized with both methods were pressed at 98.1 MPa, into 8 mm × 2.5 mm pellets, using a cold isostatic press. The samples were sintered at 1300 °C for 2 h (in the tube furnace "Lenton", UK). The heating rate was 10 °C min^{-1}, with natural cooling in air atmosphere.

Characterization of the obtained samples was carried out by:

- the X-ray diffraction (XRD) data for barium titanate powders and for sintered samples were measured using Cu Kα radiation and a graphite monochromator (Model Phillips PW1710 diffractometer) under the following experimental conditions: 40 kV, $10° < 2\theta < 120°$, with a step size of 0.020°;
- the infrared measurements were carried out with a BOMMEM DA-8 FIR spectrometer. A DTGS pyroelectric detector was used to cover the wave number range from 50 to 4000 cm^{-1};
- the Raman measurements were performed at room temperature using the Jobin-Yvon T64000 triple spectrometer system, equipped with confocal microscope and a nitrogen-cooled CCD detector. The 514.5 nm laser line of an Ar$^+$-ion was used as an excitation source. The measurements were performed at 20 mW during 200 s in spectral range 100–800 cm^{-1};
- scanning electron microscopy (SEM, Model JOEL-5300) was used to study particle size and powder morphology of activated powders and sintered samples. The pellets were prepared by pressing at 210 MPa and sintered at 1300 °C for 2 h;
- 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. Some of the samples were observed on fracture surface;
- the ferroelectrical property of BaTiO$_3$ ceramic sample obtained by mechanochemical synthesis was confirmed on the basis of following characteristic parameter: coercive field, spontaneous and remnant polarization. Silver paste electrodes for electrical measurements were applied to the polished surfaces of 1 mm thick samples by the screen printing method. The silver paste was then polymerized at 600 °C for 30 min. The spontaneous (P_s) and remnant (P_r) polarization, as well as the coercive field (E_c), were determined by evaluating ferroelectric hysteresis loops obtained by means of a modified Sawyer–Tower circuit.[13]

3. Results and discussion

The XRD results of powders (Fig. 1) indicate the formation of cubic phase of BaTiO$_3$. The appearance of X-ray reflections at $2\theta = 22.268$; 31.645; 38.955, 45.270, 50.520, 56.135, 66.062 and 75.231 are in correlation with JCPDS standards (identified using the JCPDS files no. 31-0174), which approve that in both ways of synthesis the formation of cubic phase is obtained.

It can be observed that in the case of Pechini process, BaTiO$_3$ powder is well crystallized but in the case of mechanochemistry process, significant amount of amorphous phase was detected. The XRD results of BaTiO$_3$ samples prepared by Pechini process and calcined at 700 °C (Fig. 2a) shows the formation of pseudo-cubic phase of BaTiO$_3$, which is approved by the appearance of X-ray reflections at $2\theta = 31.49$, 38.849, 45.152, 50.729, 56.075 and 65.711. These peaks centered at 2θ, which are the strongest, can correspond to cubic ($h\,k\,l$) planes (1 1 0), (2 0 0) or (2 1 1) or to tetragonal structure ($h\,k\,l$) planes (1 0 1), (0 0 2) and (1 1 2). The room temperature transition from globally cubic to tetragonal symmetry, commonly observed for BaTiO$_3$ with increasing processing temperature (700 °C → 1300 °C),
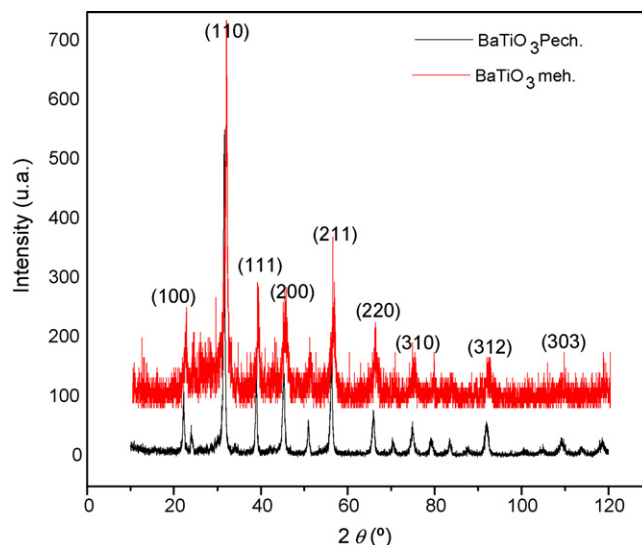

Fig. 1. X-ray diffraction patterns of the BaTiO$_3$ powders prepared (a) by Pechini method and (b) by mechanochemical synthesis.
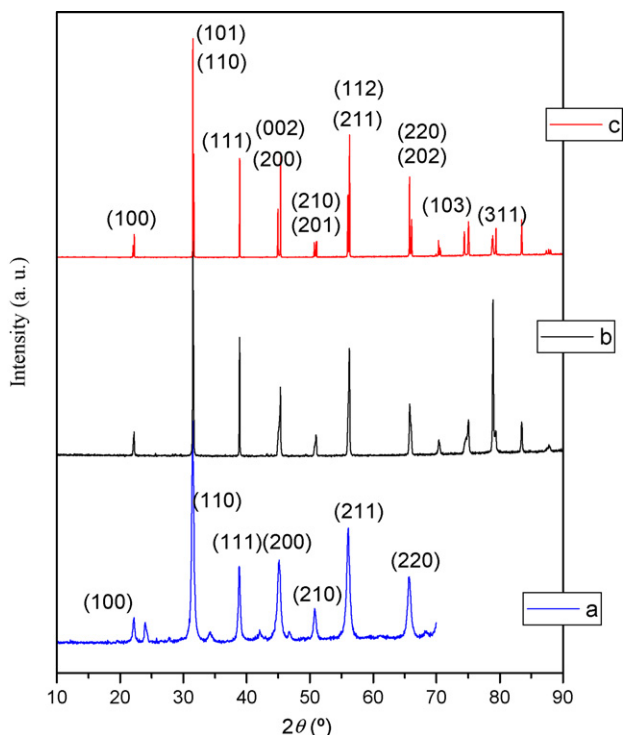
Fig. 2. X-ray diffraction $BaTiO_3$ patterns obtained on sample (a) after calcinations at 700 °C for 3 h; (b) sintered at 1300 °C for 2 h and prepared by Pechini method and (c) by mechanochemical synthesis.

is demonstrated by the gradual splitting of the pseudo-cubic $\{2\,0\,0\}$ (Fig. 2a) into tetragonal $\{2\,0\,0\}$ $\{0\,0\,2\}$ reflections in the XRD data of Fig. 2b. These splitting provide evidence for the deformation of the unit cell of $BaTiO_3$ from cubic to tetragonal (JCPDS files no. 5-0626). A slight long-range tetragonal lattice distortion first starts to appear in materials heat treated at >700 °C. Higher temperatures, 1300 °C are necessary to develop the net 1% c-axis cell elongation normally associated with the ferroelectric transition. As mentioned previously, many authors have analyzed, in considerable detail, XRD data taken

from material undergoing this evolution in lattice structure. For the sintered $BaTiO_3$ ceramic sample (at 1300 °C) prepared by Pechini process and mechanically assisted synthesis the tetragonal phase is predominantly present (Fig. 2b and c). The effect of the way of synthesis can be detected after carrying out thermal treatments on the samples.

Raman spectroscopy is one of the useful methods for investigating phase transformation behavior. There are Raman active lattice vibration modes in the tetragonal $BaTiO_3$ ($P4mm$), while there is no Raman active mode in the cubic $BaTiO_3$ ($Pm3m$).[14,15] Raman spectrum of the sample sintered at 1300 °C has the characteristic features of the $BaTiO_3$ tetragonal phase: a broad peak at about $264\,cm^{-1}$ [A_1(TO)], a sharp peak at $307\,cm^{-1}$ [B_1, E(TO + LO)], an asymmetric peak at $514\,cm^{-1}$ [A_1(TO), E(TO)] and a peak at $718\,cm^{-1}$ [A_1(LO), E(LO)].[16] The observed Raman modes are assigned to more then one phonon mode since several modes have very close frequencies and it is not possible to distinguish them from the unpolarized spectra of the polycrystalline samples.[16,17] A small dip at $180\,cm^{-1}$ (*) can be attributed to the enharmonic coupling among three A_1(TO) phonons.[16,18] In a case of ceramic sample calcined at lower temperature (700 °C) the Raman modes at 520, 715 and $719\,cm^{-1}$ are significantly broader due to lower crystalline and higher strain and amorphisation in this sample. The peaks at 307 and $264\,cm^{-1}$ diminished and the spectra below $300\,cm^{-1}$ became fluctuated indicating an incomplete crystallization.[19] The three Raman modes at ~143, 190 and $639\,cm^{-1}$ (labeled with arrows in Fig. 3a) can be ascribed to the presence of TiO_2 anatase phase[20] usually detected in the samples with lower crystalline.[16] In Fig. 4b are presented the Raman spectra of the samples obtained by Pechini method compared with a $BaTiO_3$ sample produced mechanochemically. As can be seen from Fig. 3b, the band width of the Raman mode at 717–720 cm^{-1} is significantly broader in sample prepared by mechanochemically compared to the samples obtained by Pechini. Such a behavior is consistent with the conclusion extracted from XRD spectra that the sample prepared by Pechini method is better crystallized. Besides the main Raman mode of $BaTiO_3$ mode at $520\,cm^{-1}$
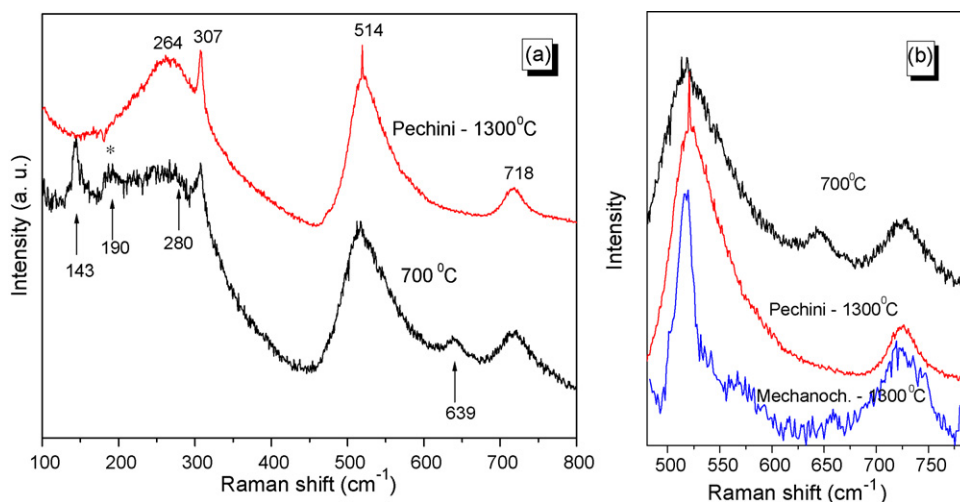

Fig. 3. (a) Raman spectra at room temperature of $BaTiO_3$ samples obtained by Pechini method, sintered at two different temperatures and (b) compared with Raman spectra of the $BaTiO_3$ sample produced by mechanochemical synthesis.
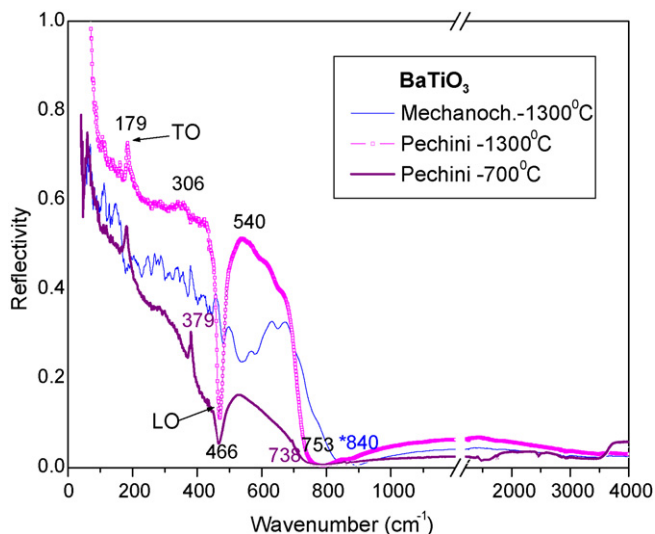
Fig. 4. IR spectra of the BaTiO₃ ceramic powders synthesized (a) by Pechini at 700 °C, (b) by Pechini and (c) by mechanochemical synthesis and sintered at 1300 °C.

Fig. 5. The microstructure of BaTiO₃ powders synthesized (a) by Pechini and (b) by mechanochemical process.

there is additional mode at ∼560 cm⁻¹ which does not belong to BaTiO₃ structure. This can imply that in mechanochemical sample there are some residuals originating from the starting oxides.

Fig. 4 shows the IR spectra of BaTiO₃ for both synthesis routes. The IR spectra of the samples are composed of a main couple of strong bands in the region 50–4000 cm⁻¹. In the case of the sample BaTiO₃ calcined at 700 °C the higher frequency band is observed at 520 cm⁻¹ with a shoulder at 738 cm⁻¹, while the lower frequency band is observed just at 400 cm⁻¹ with a shoulder at 440 cm⁻¹. This spectrum agrees with the IR spectrum of tetragonal BaTiO₃ powders reported by several authors that is somewhat variable, in relation to the particle size, shape, and aggregation.[21] A broad band at about 520 cm⁻¹, which is typical of the Ti–O vibrations in the BaTiO₃ compound, starts to be developed. In the case of the sample BaTiO₃ prepared by Pechini process and calcined at 700 °C and sintered at 1300 °C there are two extra peaks at about 179 cm⁻¹ (TO) and 466 cm⁻¹ (LO), which could be assigned to bands of the barium oxide–titanium oxide system and they had been reported only by Duran et al.[22] A similar IR spectrum was observed by Sanjurjo et al.[23] It can be observed that in the case of mechanochemistry process, significant line noise was detected. These are in excellent agreement with the corresponding measurements in the XRD. It can be concluded that frequency band strongly depends on the sample preparation.

Fig. 5 shows the SEM photographs of the BaTiO₃ synthesized by Pechini (Fig. 5a) and mechanochemically (Fig. 5b). 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 comparison with powder obtained by Pechini method where primary particles are spherical. The primary particle size
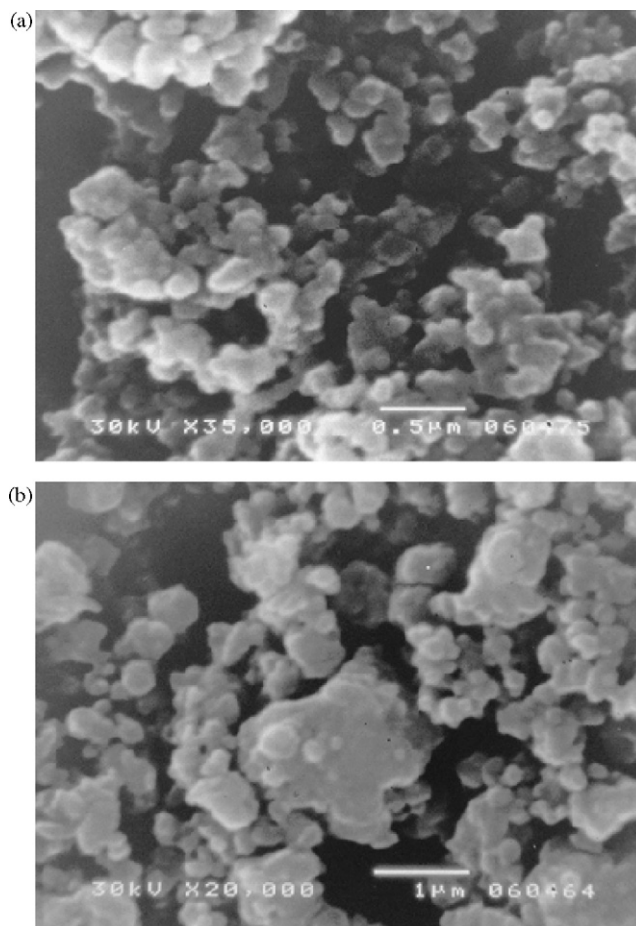
is approximately 40–80 nm and 200–250 nm for Pechini and mechanochemical process, respectively.

According to BET analysis, the specific surface area of BaTiO₃ powders prepared by Pechini was about 13.47 m² g⁻¹ and for other method 4.42 m² g⁻¹. The calculated equivalent particle size from the expression $D = 6/\rho \, SSA$ (D—is average diameter of spherical particles, SSA—the surface area of obtained powders and ρ—the theoretical density of BaTiO₃) for Pechini and mechanochemical method was about 70 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 h for both type of powder synthesis is given in Fig. 6. The average grain size of sintered sample prepared by Pechini method is around 400 nm, grains have rounded shape and approximately same dimensions indicating the homogeneous microstructure. In the case of BaTiO₃ 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.
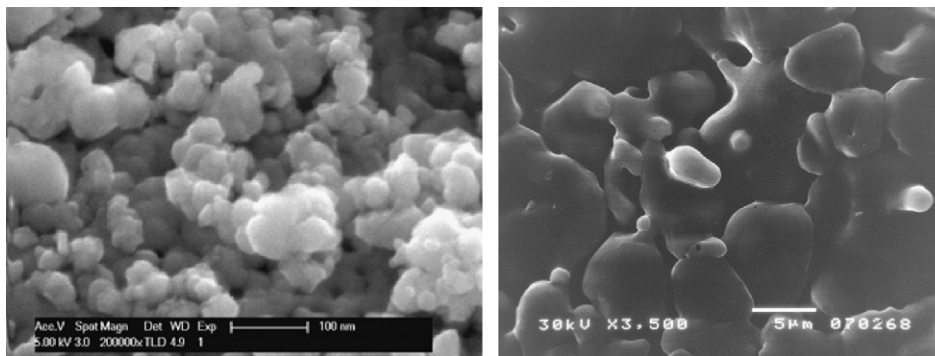
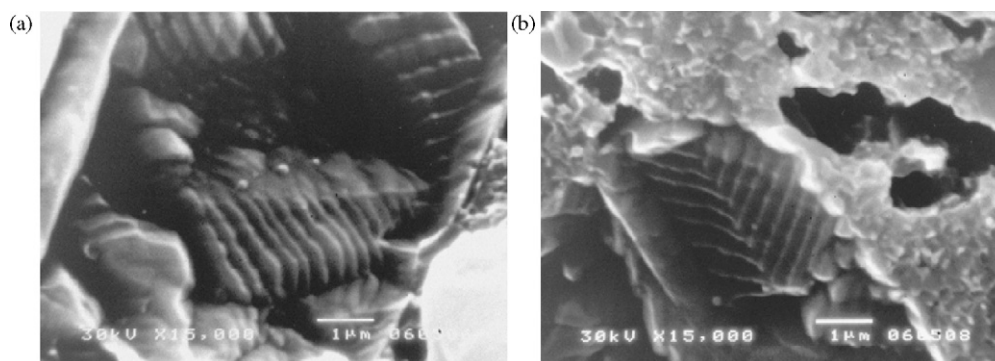Fig. 6. SEM image of the sample BaTiO$_3$ sintered at 1300 °C for 2 h.

Fig. 7. SEM micrograph of two types of domain structure of BaTiO$_3$ prepared by Pechini process and sintered at 1300 °C for 2 h.

Obtained microstructures indicate that the Pechini 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 to 16. This high grain growth factor is probably associated with a degree of agglomeration of the BaTiO$_3$ powder.

Fig. 7 represents the SEM photographs of BaTiO$_3$ prepared by Pechini process, sintered at 1300 °C for 2 h and etched in 10% HCl with 5% HF for 60 s. It is observed as two types of domain configuration. The fine parallel lines were identified as 90° walls (Fig. 7a) and the herringbone pattern (Fig. 7b) which is described as 180° walls separating the regions with different polarization.[20] The wall thickness ranges from 0.08 up to 0.14 μm and from 0.14 up to 0.17 μm for 90° and 180° domains, respectively. The domain width is around 0.20 μm for both types of domains.

It could be noticed that hysteresis loop for the BaTiO$_3$ obtained by mechanochemically is very well performed with regular shape typical for ferroelectric materials (Fig. 8). The remnant polarization was 2 μC cm^{-2} and the coercive field was 1060 kV cm^{-2}. The obtained values pointed to the regular microstructure of sintered specimens with small nanosized grains.
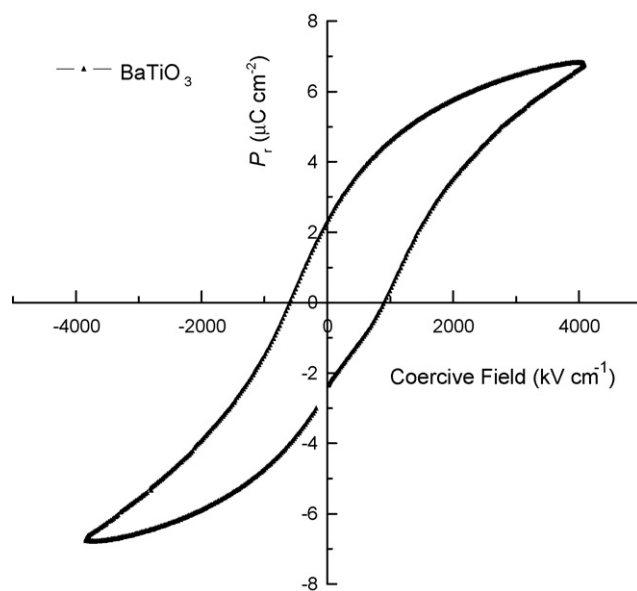

Fig. 8. The hysteresis loop of the sample BaTiO$_3$ obtained by mechanochemical synthesis and sintered at 1300 °C.

4. Conclusions

Barium titanate was prepared by two methods, polymeric organometallic precursors process and mechanochemically. In both ways of synthesis the formation of cubic phase is obtained. It can be observed that in the case of Pechini process BaTiO$_3$

powder is well crystallized but in the case of mechanochemistry process, significant amount of amorphous phase was detected. The sintered samples at 1300 °C for 2 h, prepared by Pechini and by mechanochemical process, shows the formation of tetragonal phase. The morphology of the powders consists of particles and its agglomerates, their dimensions depend of the synthesis method. The powder prepared mechanochemically posses more agglomerates. The particles are bigger and with irregular shape. Average particle size is about 100 and 250 nm for Pechini and mechanochemical process, respectively. It can be observed that with increasing temperature (700 °C → 1300 °C), XRD profiles, Raman and IR spectra exhibited the characteristic of the tetragonal phase. Also, in sintered samples, prepared by Pechini process, at 1300 °C for 2 h is observed two types of domain configuration. The wall thickness ranges from 0.08 up to 0.14 μm and from 0.14 up to 0.17 μm for 90° and 180° domains respectively. The domain width is around 0.20 μm for both types of domains. $BaTiO_3$ sintered at 1300 °C exhibits a hysteresis loop, confirming that the synthesized material possesses ferroelectric properties.

The PPM route (Pechini) 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 can also 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.

From this research it is successfully approved for the formation of a pure $BaTiO_3$ powder by both methods of synthesis and the influence of used method on $BaTiO_3$ properties is also observed.

Acknowledgements

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