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# Solid-State Mechanochemical Syntheses of Perovskites

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Additional information is available at the end of the chapter

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## Abstract

The chapter presents the possibility of applying high-energy ball milling techniques to carry out the synthesis of ceramics with perovskite structure, thereby eliminating prolonged use of high temperatures in their preparation.

On the examples of alkaline-earth metal perovskites, an influence of the most significant parameters of mechanochemical treatment on their forming process and product quality was illustrated. For the first time, it was done that the contamination of the product derived from the attrition of the grinding media and internal parts of the vial can constitute modifiers of the functional properties of produced electroceramics.

Dielectric characteristics of mechanochemically produced materials as well as using high-temperature solid synthesis were compared.

**Keywords:** Mechanochemistry, High-energy Ball Milling, Perovskites, Complex Oxides, Electroceramics

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## 1. Introduction

The family of chemical compounds with perovskite-type structure due to the unique electrical properties comprises a broad range of electrotechnical materials – dielectrics by semiconductors, superionic conductors, conductors with combined ionic and electron conductivity to high-temperature superconductors [1, 2].

Moreover, as is known, these compounds in certain temperature ranges have piezoelectric, pyroelectric, ferroelectric, antiferroelectric, paraelectric, ferromagnetic, or paramagnetic properties [3–6]. Also important is the simplicity of their crystalline structure, chemical composition, and the synthesis of these compounds in monocrystalline or polycrystalline form. It is easy to modify the structure and thus the properties of perovskites. Even a slight change of their ideal crystal structure and chemical composition may result in the appearance of new,

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not only electrical but also other, properties such as catalytic or mechanical. Therefore, it is very important to select the method of their production. The synthesis of polycrystalline titanates with perovskite structure, due to the fact that these compounds are hardly fusible materials, is carried out at high temperatures by solid-phase reaction. However, such a temperature causes the appearance of sinters and agglomerates what hinder fine crystalline product formation. This is extremely important because the morphology and grain size in electroceramics directly affects on their properties [7–12]. This problem can be solved by different ways, e.g., using a sol–gel method [13]. This technique owing to the thorough mixing of the precursor materials in solution and the relatively lower temperature of crystallization (1,200 K) allows to obtain a homogenous material with small, fine crystals and excellent chemical stoichiometry. Unfortunately, the sol–gel method is complex and requires advanced, very clean equipment, and organometallic reagents that are not only expensive but also environmentally hazardous. There are also known other synthesis techniques such as co-precipitation or hydrothermal methods. However, many of these methods enable to synthesize perovskite-type ceramics with fine crystals; they are unpopular because their complexities and costs preclude their use in a large-scale industrial fabrication [14–20]. Alternatively, this kind of ceramics can be produced by high-energy ball milling at room temperature [21–28]. This technique leads to the activation and/or synthesis of new compounds. Activation of solid powders in this case is based on the high degree of fragmentation and a large number of structural defects. However, in order to obtain the crystalline milling products, sometimes the subsequent heat treatment is needed. Then, much lower temperature may be used than in conventional methods. Moreover, using the mechanochemical method, it is possible to control the grain morphology of ceramics by selection of appropriate process parameters. Such a simplicity and large control of process parameters make it an excellent alternative to expensive and complex manufacturing techniques of advanced ceramic materials.

## 2. General aspects of mechanochemistry

The essence of mechanical treatment is the impact of moving grinding media with grains of ground material and the interaction between the grains of powder. During these processes depending on the type of the mill and the applied milling parameters, the energy supplied to the material is in the range of 0.1 to 100 MJ/kg. Transfer of this energy is precisely localized in the collision zone at the moment of the collision between the grinding media. During the collision, the kinetic energy of the grinding media is absorbed by a small volume (approx. 1 mm<sup>3</sup> of ground powder) and is immediately converted into elastic energy. Resulting stresses cause the destruction of the ground material. Depending on the physical nature of the ground powder, mainly hardness and thermodynamic conditions, the cracks of crystals occur, resulting in the reduction of the grain size, and/or a mutual merging of the particles.

All these phenomena intensify the diffusion processes in solids accelerating the chemical reactions. It is caused by the forces of collisions, strike/hit, compression, and friction occurring between the grinding media and the ground material and between the grinding media and the walls of the reactor [29–35]. In consequence, the reactions take place without the need of

diffusion of substrates through the product layer because interfacial contact of ground materials is periodically renewed.

## 2.1. Process parameters of mechanochemical treatment

Fabrication of different materials by a mechanochemical treatment is a complex process because it is influenced by many factors. Generally, they are connected with energetics and/or the environment of milling. The amount of energy supplied to the material during mechanical treatment mainly depends on the type of mill. There are various kinds of construction solutions of the mills [31, 36–37]. The type of mill should be chosen taking into account the advantages and disadvantages of each device. The decisive parameter for the kinetics of the mechanochemical processes is the rotation speed of the reactor [38]. The rotation speed or impact, in the case of vibratory mills, transfer directly into interaction frequency of grinding media with powder particles and their speed inside the reactor. Milling energy highly depends on the BPR factor (*ball to powder ratio*), which expresses the ratio (e.g., mass) of grinding media to the ground material. Although this relationship is not linear, this is related to the degree of the reactor filling with balls (a large number of them makes the movement of the balls more complex) [29, 39]. Grinding media lose their energy due to frequent collisions among themselves. Too small or too large volume of ball in the vial reduces the efficiency of the milling process. It should be pointed that both high speed and the large number of balls cause increase in the reactor temperature. Higher temperature can be beneficial to the phenomenon, stimulates the diffusion of the atoms in the solids, and also increases the degree of ductility of the steel, which leads to a faster wear. All parameters relating to energetics of the grinding unit should be taken into account when planning the mechanical treatment process.

The selection of the process parameters directly affects the properties of the obtained phases. Depending on the desired final effect of high-energy, ball milling can/must be used different time, the atmosphere, and the medium of mechanochemical treatment. Determination of mechanochemical synthesis duration is rather simple – depends on the time required to form the desired phases. The processes associated with mechanical activation of solids, such as structure modification, deposition of active catalytic phase on carrier or simple comminution need own individual milling time, therefore it must be selected experimentally.

Mechanochemical processes are often carried out under a protective atmosphere or in vacuum. This prevents milled material from the additional reactions with air components such as oxygen or nitrogen. Negative phenomenon of agglomeration of grains as a result of high-energy milling process can be reduced by using water or alcohol as a medium [21, 40–52].

The kinetics of mechanochemical reactions can be also controlled through various types of precursors. This is particularly important in the case of exothermic reactions, which very often have an explosive nature (SHS reaction) as in the case of metallothermic processes [53–55]. The use one of the substrates not in the form of oxide (i.e., as a ready reactant) but as hydroxosalt or carbonate needs heat to its stepwise decomposition into the oxide (endothermic process), increasing the time of availability of the reagent for the synthesis. This type of process is called by Avvakumow [56] as "soft mechanochemistry".

### 3. Direct mechanochemical syntheses of titanates

The continuous desire to limit great inconvenience to the natural environment and the cost of preparation of a variety of functional materials and the need for materials with more "sophisticated" properties makes the mechanochemical treatment an interesting alternative technique to the conventional ones. The possibility of applying this method for the preparation of high-quality ceramic materials with perovskite structure is presented below. In Figures 1 and 2 are shown the influence of various process parameters of high-energy ball milling and the nature of the reactants on the dynamics and properties of the obtained products, respectively.

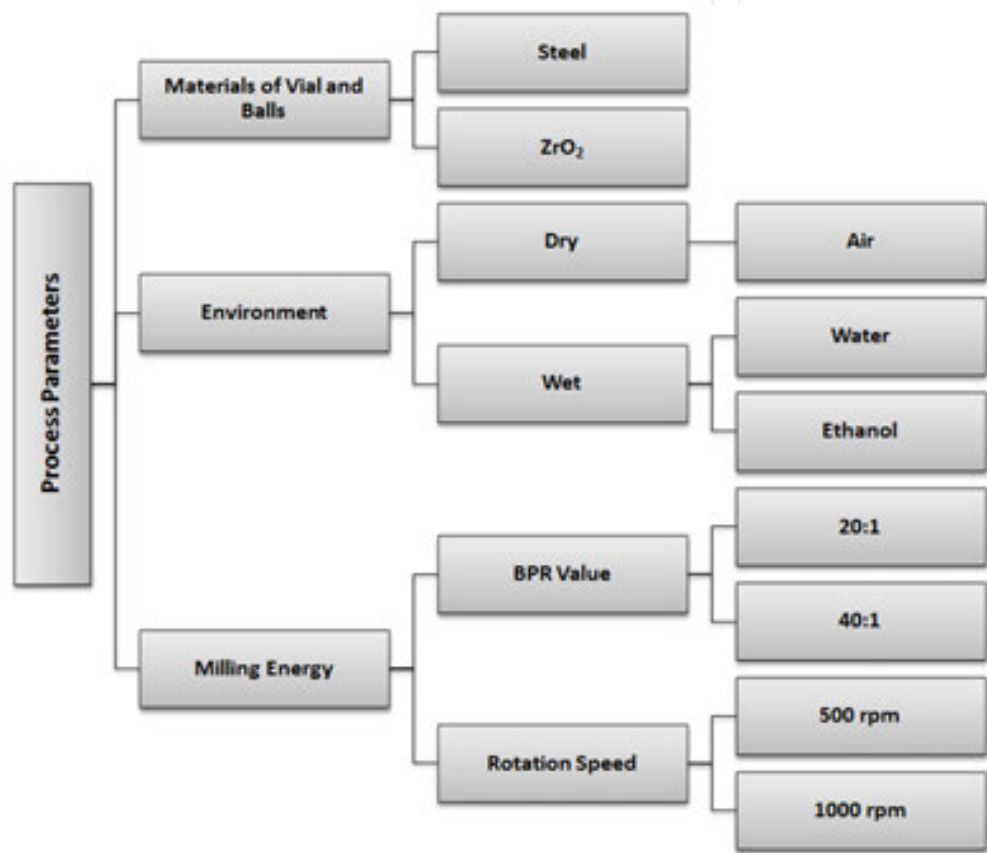
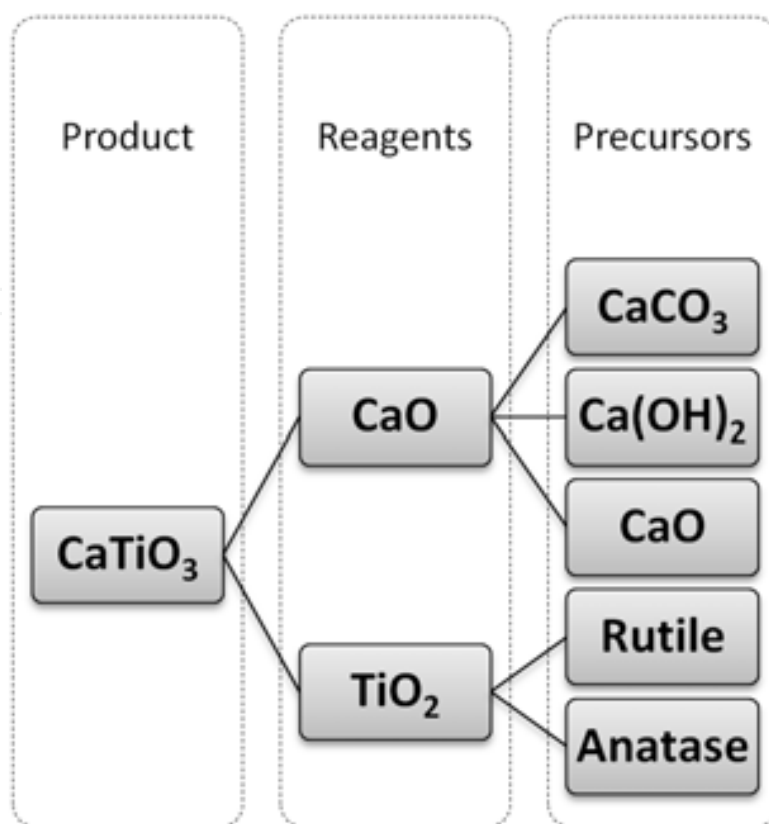


Figure 1. Various milling conditions in mechanochemical syntheses of perovskites

### 4. Syntheses of perovskites of alkaline earth metals – MTiO<sub>3</sub> (M = Ca, Sr, Ba)

#### Mechanochemical synthesis of calcium titanate

Synthesis of compounds with perovskite structure in the system CaO-TiO<sub>2</sub> is carried out in the solid phase without the need of high-temperature processing (for processing details – see:



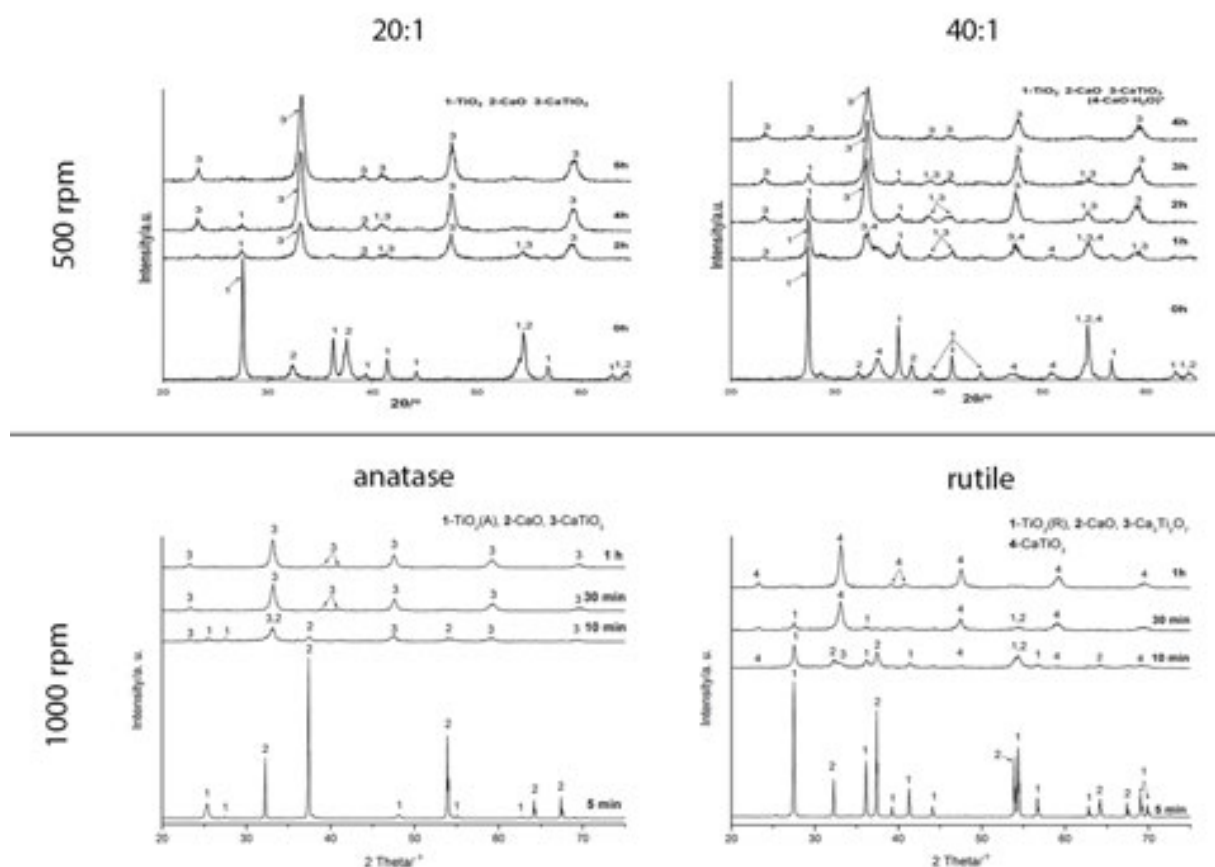
**Figure 2.** Different oxides' precursors to syntheses of complex oxides ( $\text{CaTiO}_3$ )

Appendix A1). However, the formation of a crystalline product is highly conditioned by several milling process parameters (see: Section 2.1). The influence of parameters relating to milling energy, such as the BPR value and rotation speed on the product formation time, is illustrated in Figure 3. It is worth to pay attention to the synthesis time, which using the appropriate conditions can be only about 1 h, i.e., substantially shorter than the other methods of synthesis.

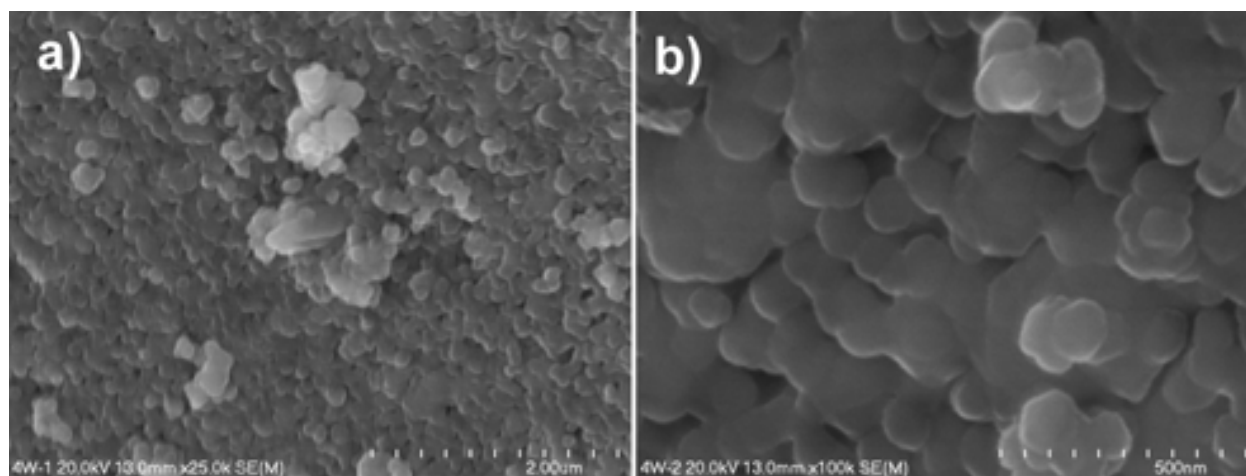
Decrease in the values of rotation speed or BPR parameter increases the synthesis time. The type of  $\text{TiO}_2$  (rutile or anatase) is also important for the kinetics of process. Mechanochemically obtained calcium titanate is characterized by grain size less than 100 nm and good homogeneity in terms of particle size. In this case, it is not necessary to make the subsequent high-temperature treatment process, which eliminates the problem of agglomerates formation and an excessive non-uniform grain growth (Figure 4). This has a meaning for properties (e.g., a ferroelectric or catalytic) of materials.

Commonly used wet environment, during the high-energy ball milling (ethanol or water), in order to reduce the negative phenomenon of agglomeration acts negatively on the course of the synthesis reaction because of hindering the reactants' phase contact. However, high-energy milling activates the reactants by particles size reduction and creation of the crystal defects which facilitates the diffusion of atoms, lowering the temperature of subsequent calcination process (see Figure 5).



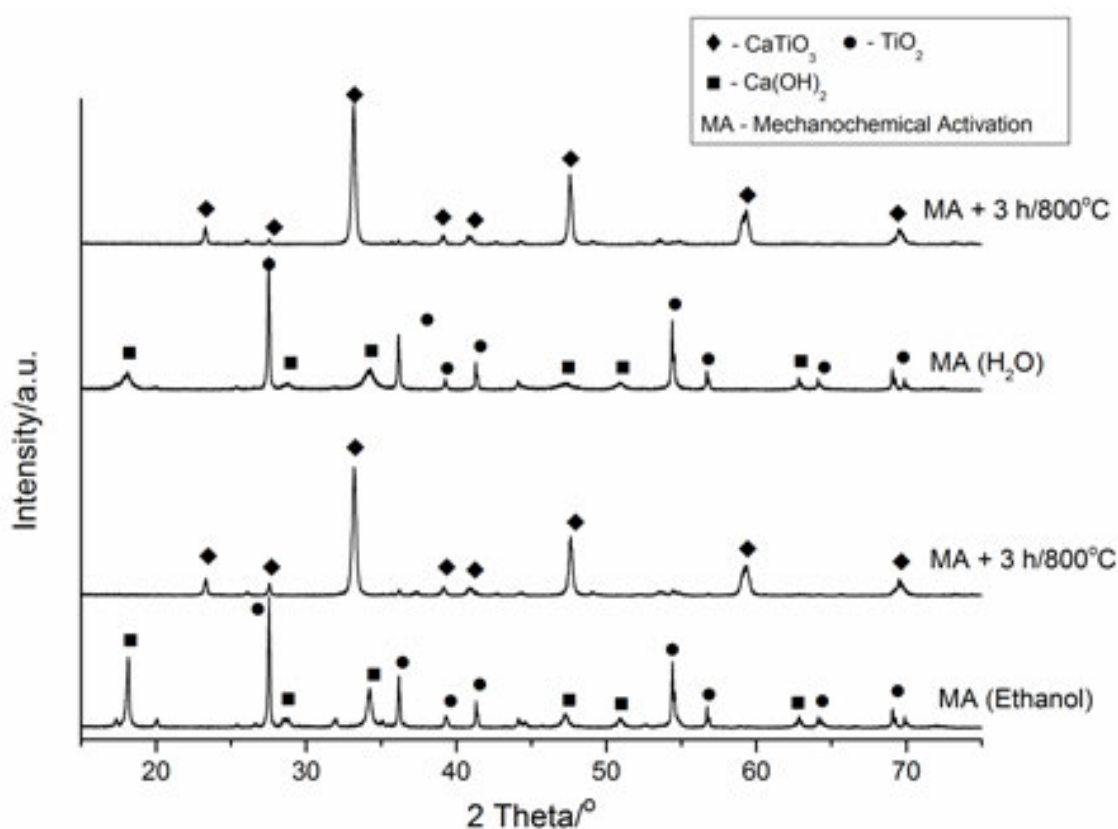


**Figure 3.** XRD patterns of calcium titanate – illustration of milling conditions (BPR = 20:1 and 40:1; rpm = 500 and 1000) and two forms of  $\text{TiO}_2$  for  $\text{CaTiO}_3$  synthesis

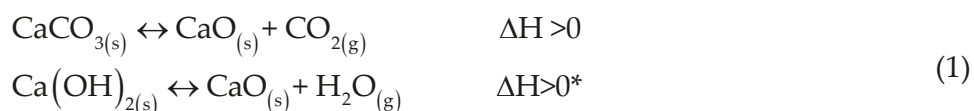


**Figure 4.** SEM images of mechanochemically synthesized  $\text{CaTiO}_3$ ; (a) and (b) – different magnification

In the systems of  $\text{CaCO}_3\text{-TiO}_2$  and  $\text{Ca(OH)}_2\text{-TiO}_2$ , synthesis is much more difficult. It is a consequence of two reactions: (1) and (2) or (1\*) and (2). Synthesis is limited by the decomposition rate of carbonate or calcium hydroxide to the oxide.



**Figure 5.** XRD patterns of CaO-TiO<sub>2</sub> system after mechanochemical activation in different media (water and alcohol) and subsequent calcination



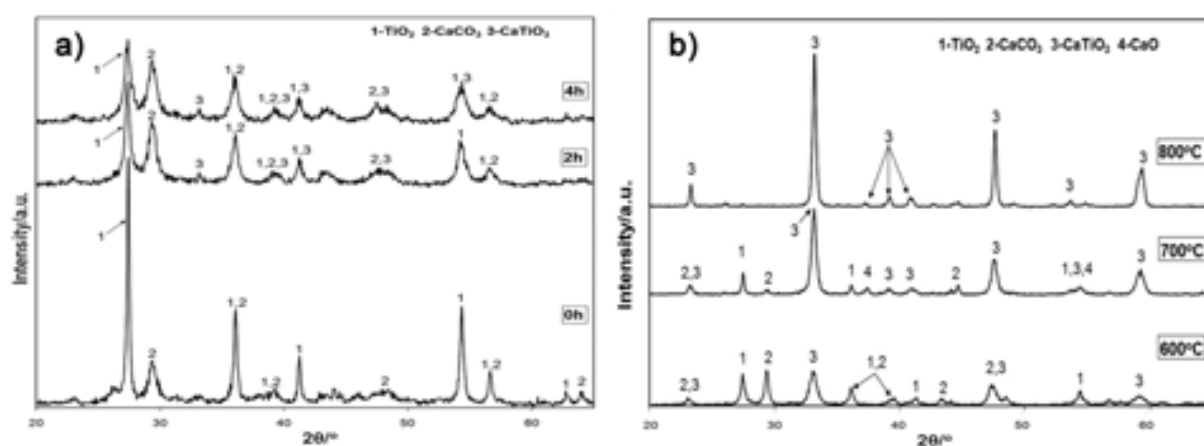
The example of mechanochemical synthesis of calcium titanate in CaCO<sub>3</sub>-TiO<sub>2</sub> system is presented in Figure 6.

As can be seen, in order to obtain a monophasic product after 4 h of milling, a subsequent heat treatment at 800°C was necessary to use [40].

The preparation of other alkaline-earth metal titanates, e.g., barium and strontium, by a mechanochemical synthesis proceeds in analogy to the above-mentioned CaTiO<sub>3</sub> example.

The abovementioned experimental results indicate that the method of mechanochemical synthesis may be used to produce high-quality perovskite ceramics. Thus, short time of the synthesis, the use of substrates in the oxide form, and a lack of using the high-temperature treatment significantly reduce both manufacturing costs and negative influence on environment.





**Figure 6.** XRD patterns of calcium titanate formation: (a) up to 4 h of milling, (b) subsequent calcination at different temperatures

## 5. Modification of perovskite-type electroceramics properties

Apart from the rapid and relatively simple synthesis of perovskite compounds, mechanochemical method also allows to modify their chemical and physical properties. Such modifications can be made by changing the chemical composition of perovskites, production of ceramics of an adequate morphology (grain size, defected, etc.), and also using as additives the contaminations originating from wear down of the grinding media (Examples 1–3).

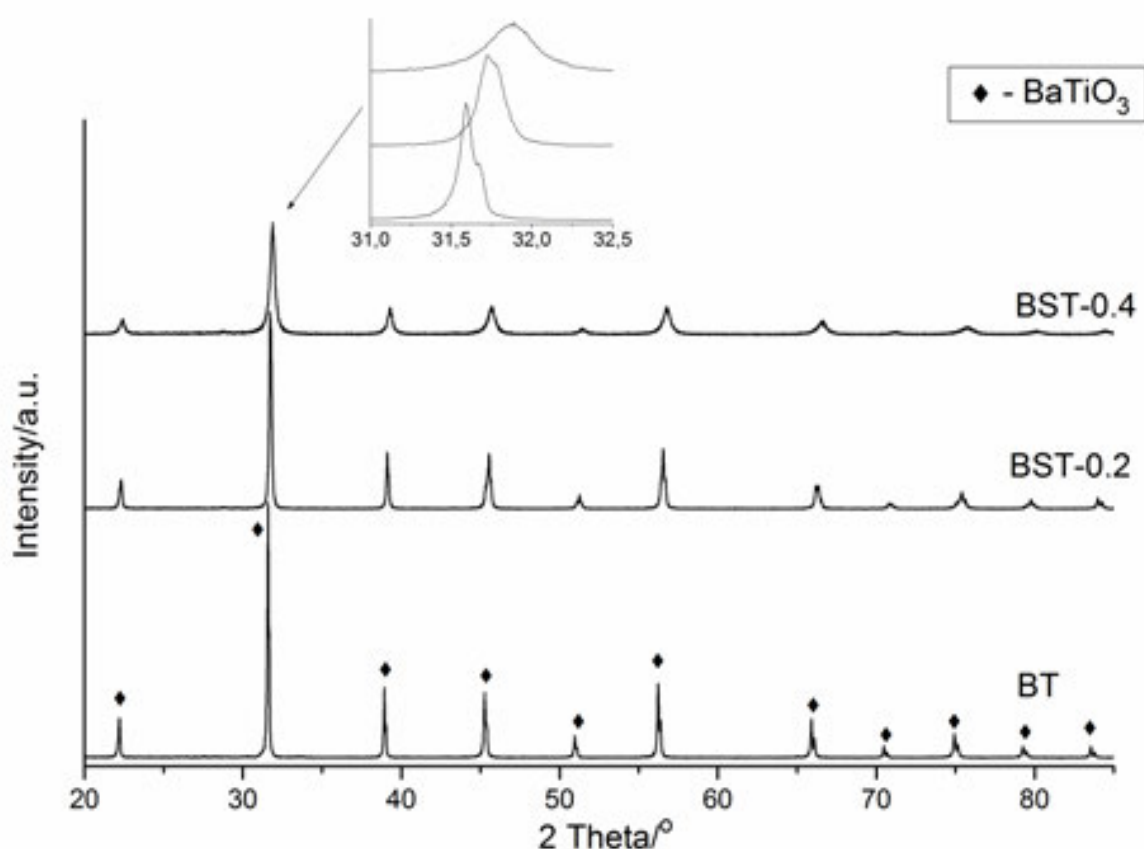
### 5.1. Formation of solid solution by doping various cations

#### Example 1. $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ( $0.0 \leq x \leq 0.4$ )

XRD patterns of the synthesized compounds are shown in Figure 7. They indicate the influence of the presence of  $\text{Sr}^{2+}$  on the crystallinity of products. Any phase of strontium oxide was found even in the case of strontium concentration equal to  $x = 0.4$  in  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ .

Different ionic radii of  $\text{Ba}^{2+}$  (1.36 Å) and  $\text{Sr}^{2+}$  (1.16 Å) induce distortion of lattice. A close look at a slow scan of reflection (e.g., from  $31.0^\circ$  to  $32.5^\circ$ ) shown as an inset which indicates that there is a slight shift of this reflection to higher  $2\theta$  angles. This confirms the substitution of  $\text{Sr}^{2+}$  ions in the  $\text{BaTiO}_3$  lattice. It might be concluded that single phases of  $\text{BaTiO}_3$ ,  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ , and  $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  can be successfully prepared by the high-energy ball milling process. (Synthesis conditions – see: Appendix A2)

Below it is shown an additional excellent example that, in the case of mechanochemical synthesis, should not be based on results from only one technique. The negative phenomenon of agglomeration, often occurring during milling, may affect the interpretation of the particle size and specific surface area of the material. Performed for all solid solutions, the analysis of the of particle size distribution by laser diffraction method showed that in each case about 10 microns is the dominant fraction. The specific surface area measurements (BET method) of each solid solutions clearly indicated that this area is growing with the increasing concentra-



**Figure 7.** XRD patterns of mechanochemically synthesized  $\text{BaTiO}_3$  (BT) and  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  (BST-0.2),  $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  (BST-0.4) [59]

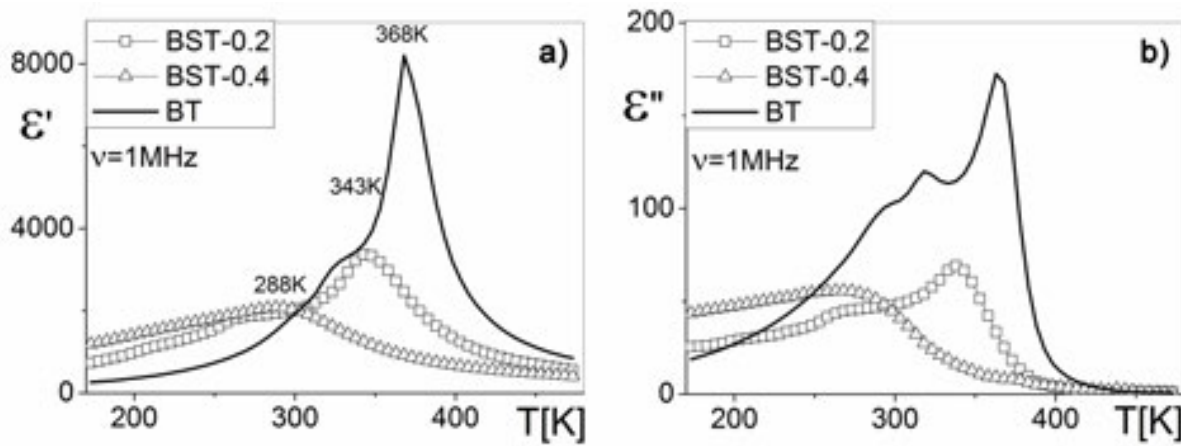
tion of modifier – from  $7.16 \text{ m}^2/\text{g}$  for pure  $\text{BaTiO}_3$  to  $34.99 \text{ m}^2/\text{g}$  for  $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  indicating on diminishing grains size. This was also confirmed by microscopic observation (SEM). The size of grains varies from 500 to approx. 100 nm.

#### *Dielectric properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$*

The dielectric properties of  $\text{BaTiO}_3$  (BT),  $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  (BST-0.2), and  $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  (BST-0.4) ceramics are described by the temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of electric permittivity. These properties were determined at selected frequencies of the electric field (1 MHz).

For the  $\epsilon'/T$  dependence (Figure 8a), with increase in the strontium concentration, the Curie temperature  $T_C$  gradually shifts toward lower value, and the peak of this transition becomes broader.

For  $\text{BaTiO}_3$  (BT) sample a classic paraelectric–ferroelectric (PE–FE) phase transition at 368 K occurs simultaneously with the change from a cubic to tetragonal structure. At lower temperature, the peak has diffused character which can be explained by the presence of small amount of impurities ( $\text{ZrO}_2$ ) from the reaction vial and grinding media. For the samples of solid solution BST-0.2 and BST-0.4, the  $\epsilon'(T)$  plots show a diffusion nature of PE–FE phase transitions. The value of  $\epsilon'$  maximum for BST-0.2 ceramics is about three times smaller and for BST-0.4



**Figure 8.** The temperature dependence of real part of dielectric permittivity ( $\epsilon'$ ) a) and imaginary part of dielectric permittivity ( $\epsilon''$ ) b) for BaTiO<sub>3</sub> (BT), Ba<sub>0.8</sub>Sr<sub>0.2</sub>TiO<sub>3</sub> (BST-0.2), and Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> (BST-0.4) samples

four times than in the case of BT sample. The phase transitions for Ba<sub>0.8</sub>Sr<sub>0.2</sub>TiO<sub>3</sub> (BST-0.2) and Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> (BST-0.4) samples occur at temperature 343 and 288 K, respectively.

The energy loss of the electric field represented by imaginary part of electrical permittivity ( $\epsilon''$ ) is tied to a structural phase change (Figure 8b). The temperature of maximum  $\epsilon''(T)$  correlates with the temperature of maximum  $\epsilon'(T)$ .

#### Example 2. (Ba<sub>1-x</sub>Na<sub>x</sub>)(Ti<sub>1-x</sub>Nb<sub>x</sub>)O<sub>3</sub> ( $0.0 \leq x \leq 0.15$ )

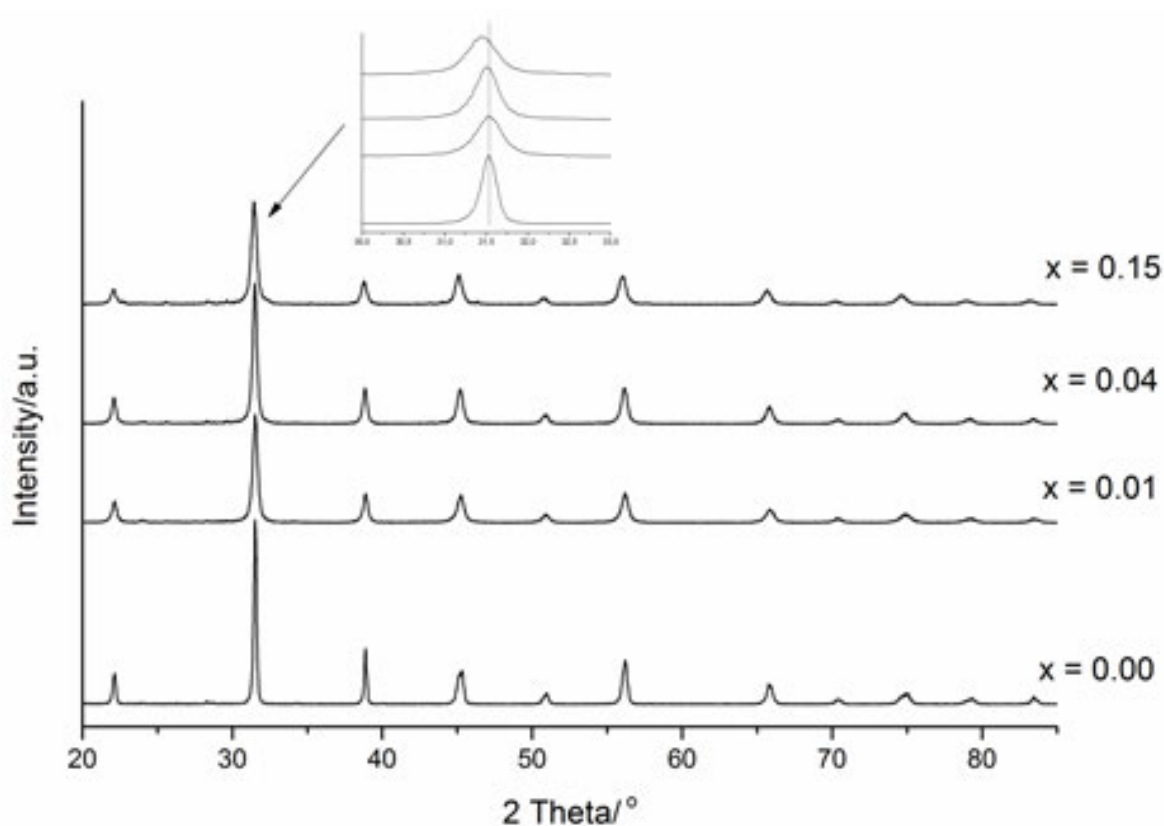
Figure 9 shows a comparison of X-ray powder diffraction patterns of BaTiO<sub>3</sub> ceramics and (Ba<sub>1-x</sub>Na<sub>x</sub>)(Ti<sub>1-x</sub>Nb<sub>x</sub>)O<sub>3</sub> for:  $x = 0.01$ ;  $x = 0.04$ ;  $x = 0.15$  obtained by mechanochemical method. Visible shifts of the main diffraction reflections confirm the formation of appropriate solid solutions. In addition, these materials are characterized by a uniform grain size, approx. 500 nm. All are characterized by clearly defined grain boundaries and the lack of sinters. The example of morphology images of these materials in comparison with ceramics synthesized by conventional high-temperature method is presented in Figure 10.

Preparation of (Ba<sub>1-x</sub>Na<sub>x</sub>)(Ti<sub>1-x</sub>Nb<sub>x</sub>)O<sub>3</sub> solid solution by conventional high-temperature solid-phase synthesis requires a long-term heating of the mixture starting materials at high temperature. Using mechanochemical method significantly reduces the synthesis time. The monophasic product was obtained after 1.5 h of high-energy milling and as in the previous example without the need for subsequent calcination.

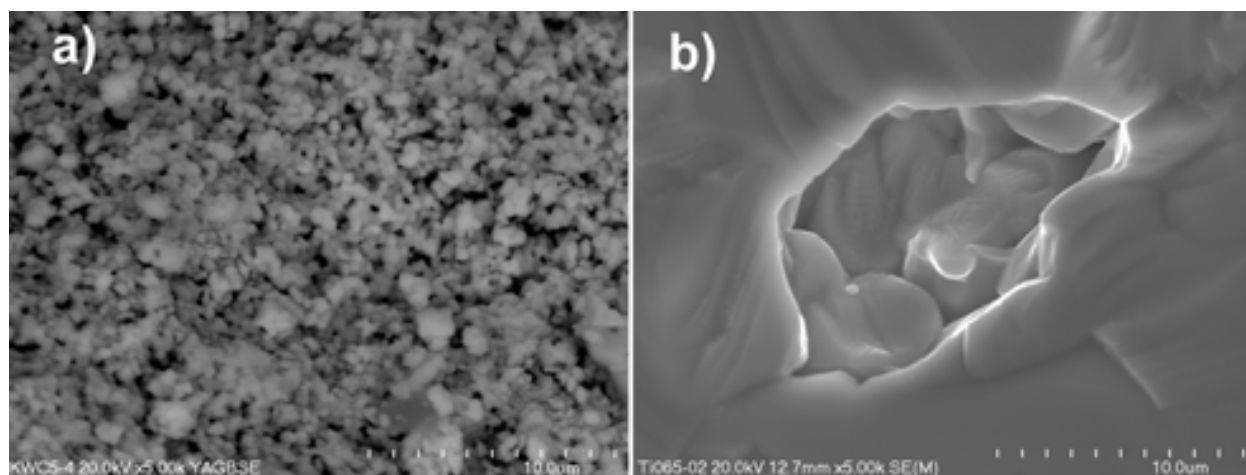
#### Dielectric properties of (Ba<sub>1-x</sub>Na<sub>x</sub>)(Ti<sub>1-x</sub>Nb<sub>x</sub>)O<sub>3</sub>

Comparing the dielectric properties of the same materials produced by two methods (Figure 11), i.e., mechanochemical and high-temperature syntheses, can draw the following conclusions:

- BaTiO<sub>3</sub> and the ceramic solid solution of BNTN<sub>x</sub> for the composition of  $x = 0.01$  are classical ferroelectrics with a sharp PE–FE phase transition.



**Figure 9.** XRD patterns of mechanochemically synthesized  $(\text{Ba}_{1-x}\text{Na}_x)(\text{Ti}_{1-x}\text{Nb}_x)\text{O}_3$  for:  $x = 0.01$ ;  $x = 0.04$ ;  $x = 0.15$  solid solutions

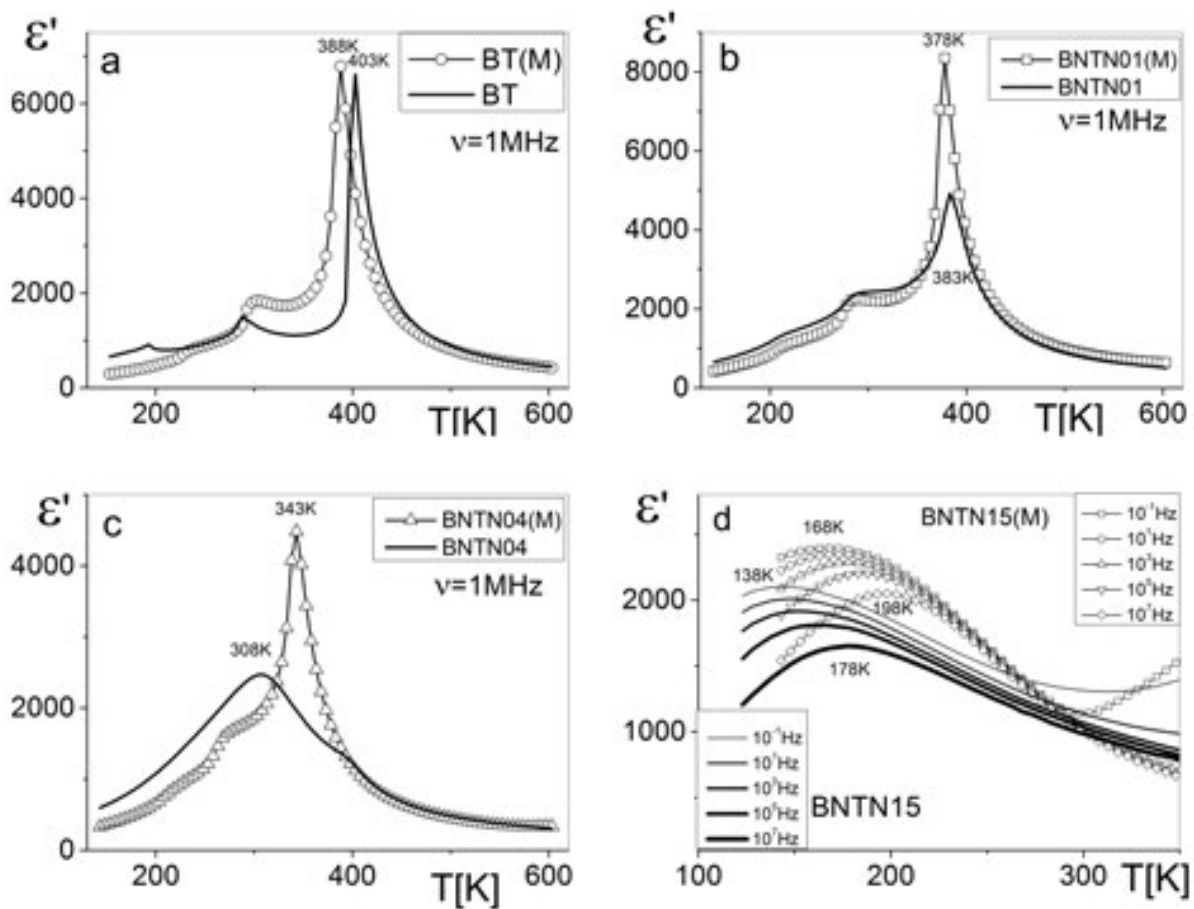


**Figure 10.** The SEM micrographs of microstructure of  $\text{BNTN}_x$  (for  $x = 0.04$ ) sample surface, (a) mechanochemical, (b) high temperature

- The increase in the value of  $x$  in the  $\text{BNTN}_x$  samples causes a diffuseness of the phase transition. Such behavior is a result of the different valency of substituted ions in both cationic sublattices.

- For composition of  $x = 0.15$ , a strong dispersion of the dielectric permittivity maximum is observed. The obtained results clearly indicate that BNTN $x$  ( $x = 0.15$ ) sample is relaxor ferroelectric.
- Materials produced by mechanochemical synthesis method is characterized by better parameters, e.g., higher value of dielectric permittivity, less diffused character of para-ferroelectric phase transition.

The quick and simple synthesis without any thermal operation and better functional properties of products show the advantages of mechanochemistry. More information can be found in the works [57, 58, 61].



**Figure 11.** The temperature dependence of the real part of the complex dielectric permittivity for (a) BT, (b) BNTN $x$ ;  $x = 0.01$ , (c)  $x = 0.04$ , (d)  $x = 0.15$  samples obtained by conventional (solid line) and mechanochemical (open symbol) methods [61]

### Example 3. Influence of impurities from the milling process on the properties of BaTiO<sub>3</sub> (A) and CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (B)

As mentioned in the chapter introduction, negative phenomenon of all processes associated with the high-energy milling is the attrition of some construction elements such as grinding



media and/or inner coating of vial. This is a significant problem to technologists because such impurities are difficult to remove from milling products.

However, this effect can be used to modify the properties of materials. By selecting a suitable material of grinding media and grinding vial, it is possible to modify for example catalytic or electrical properties of ceramics.

Possibilities of the use of such impurities from the milling process are illustrated on perovskite compounds with high technological importance, i.e.,  $\text{BaTiO}_3$  and  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . The results are presented for comparison with analogous materials produced by high-temperature solid phase synthesis.

**a.**  $\text{BaTiO}_3$

Barium titanate was prepared mechanochemically using grinding media and grinding vial made of steel and zirconium oxide. Conditions of synthesis – see: appendix A3.

In Figure 12 is presented room temperature X-ray powder diffraction for mechanochemically and high-temperature produced  $\text{BaTiO}_3$ . There are considerable differences in the intensities and in half-width of the diffraction reflexes of ceramics and indicating on the various morphologies of the grains. This is confirmed by SEM microscopic observation (Figure 13). The samples after mechanical treatment have much smaller particles (about 500 nm) in comparison to conventionally produced  $\text{BaTiO}_3$ , which is characterized by large, uneven in size and shape of the grains.

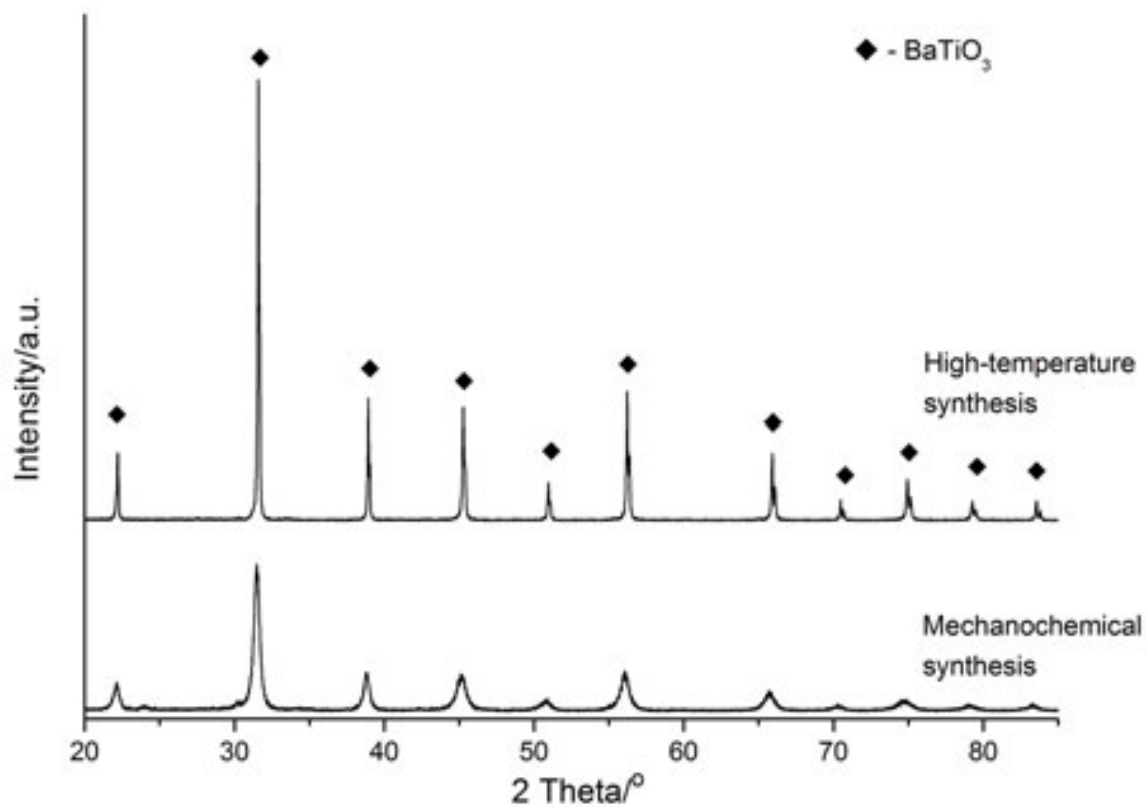
Materials prepared by these two methods also differ in terms of size BET surface area. The mechanochemically obtained powders were characterized by surface area of approx.  $7 \text{ m}^2/\text{g}$ ,  $\text{BaTiO}_3$  prepared by high-temperature synthesis due to the presence, among others, of sinters have a much smaller specific surface area of  $0.25 \text{ m}^2/\text{g}$ .

$\text{BaTiO}_3$  synthesized using the high-temperature method had tetragonal symmetry at room temperature, in contrast to that obtained mechanochemically, which was cubic. The high degree of commutation and the large number of defects caused by high-energy ball milling limits long-range order in the crystallographic structure, and this prevents phase transitions. Calcination of the powder for 1 h at 1,373 K eliminates this problem [21].

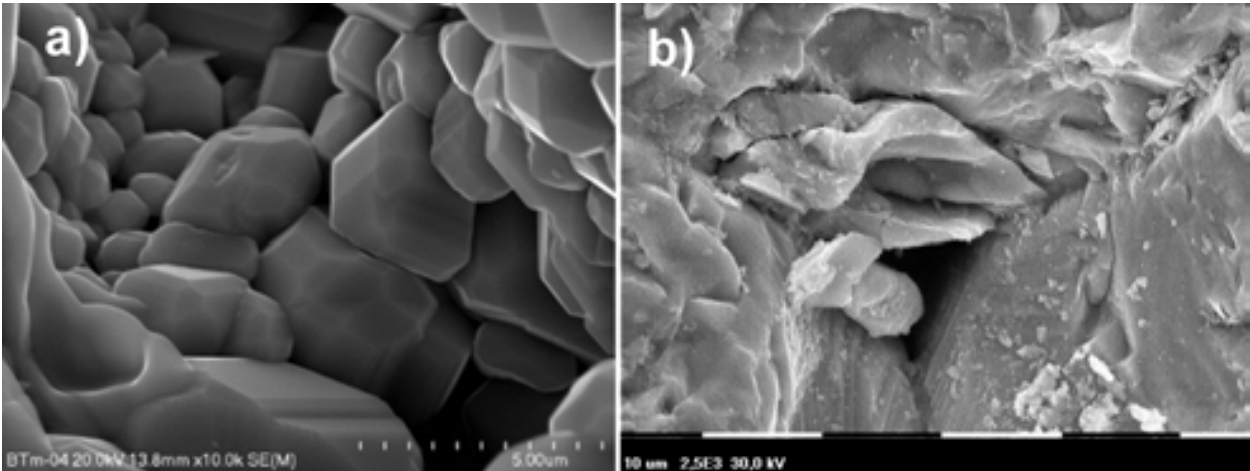
The amount of impurities – in both cases the iron or zirconium oxide – in samples prepared mechanochemically was approx. 1% wt. Because the barium titanate is a model ferroelectrics, below is illustrated the effect of the presence of these impurities on these properties. Figure 14 presents the temperature dependence of the dielectric permittivity for all ceramics. Samples are marked on the system as:  $\text{BaTiO}_3/\text{T}$  – high-temperature synthesis,  $\text{BaTiO}_3/\text{Zr}$  and  $\text{BaTiO}_3/\text{Fe}$  – mechanochemical synthesis.

In the case of  $\text{BaTiO}_3/\text{T}$ , the temperature at which  $\epsilon'$  is the highest represents the paraelectric–ferroelectric (PE–FE) phase transition. At all frequencies of the electric field, a classical, sharp transition can be seen at 403 K, which corresponds to a structural shift between cubic and tetragonal phases. At 288 K there is another maximum, however its value is around fourtimes smaller than the transition at 403 K. The observed temperature of this phase transition for





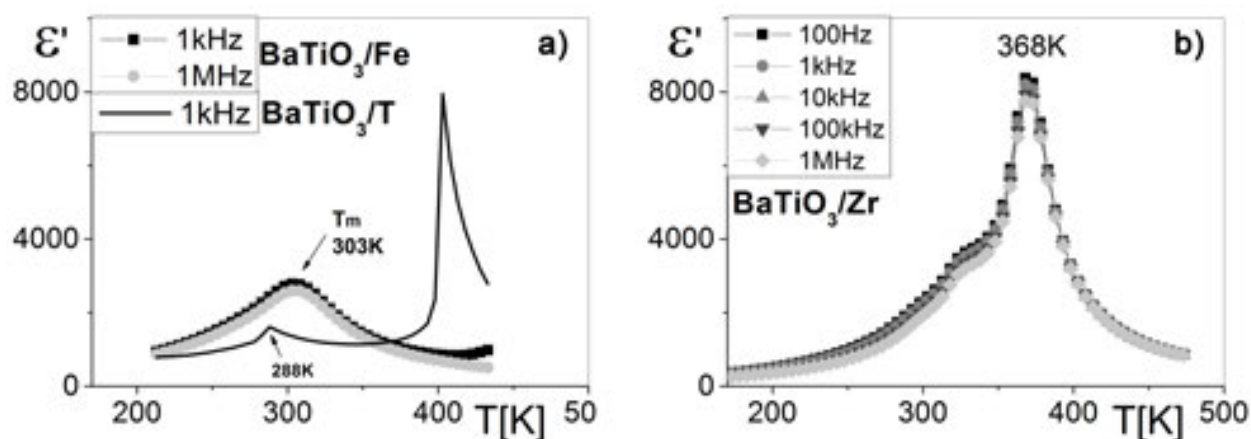
**Figure 12.** Comparison of X-ray powder patterns of BaTiO<sub>3</sub> obtained by two different synthesis methods [21]



**Figure 13.** SEM photomicrographs of BaTiO<sub>3</sub> powders obtained by (a) mechanochemical and (b) high-temperature solid-state syntheses [21]

BaTiO<sub>3</sub> varies from the literature by 5–20 K [8, 16, 17, 20]. It is possible to surmise that transition at 288 K which corresponds to a change from a tetragonal structure to an orthorhombic one.

For BaTiO<sub>3</sub>/Zr ceramics, the PE–FE transition occurs at 368 K. This transition is somewhat diffused, and the frequency of the electrical field a little bit changes the behavior of the material.



**Figure 14.** The temperature dependence of real part of dielectric permittivity ( $\epsilon'$ ) for  $\text{BaTiO}_3/\text{T}$ ,  $\text{BaTiO}_3/\text{Fe}$ , and  $\text{BaTiO}_3/\text{Zr}$  samples [21]

A further lowering of the temperature causes greater peak diffusing compared to that observed in “pure”  $\text{BaTiO}_3$ . There is no maximum observed at 288 K.

The  $\text{BaTiO}_3/\text{Fe}$  product has a characteristically diffused peak at the PE–FE transition, the most diffused of any of the samples tested. The observed maximum of  $\epsilon'$  approaches a value of 3,000 at a temperature of 303 K, nearly 100 K lower than the same transition in  $\text{BaTiO}_3/\text{T}$ . Measurements at different frequencies of electrical field show that this material does not have the properties of a relaxor.

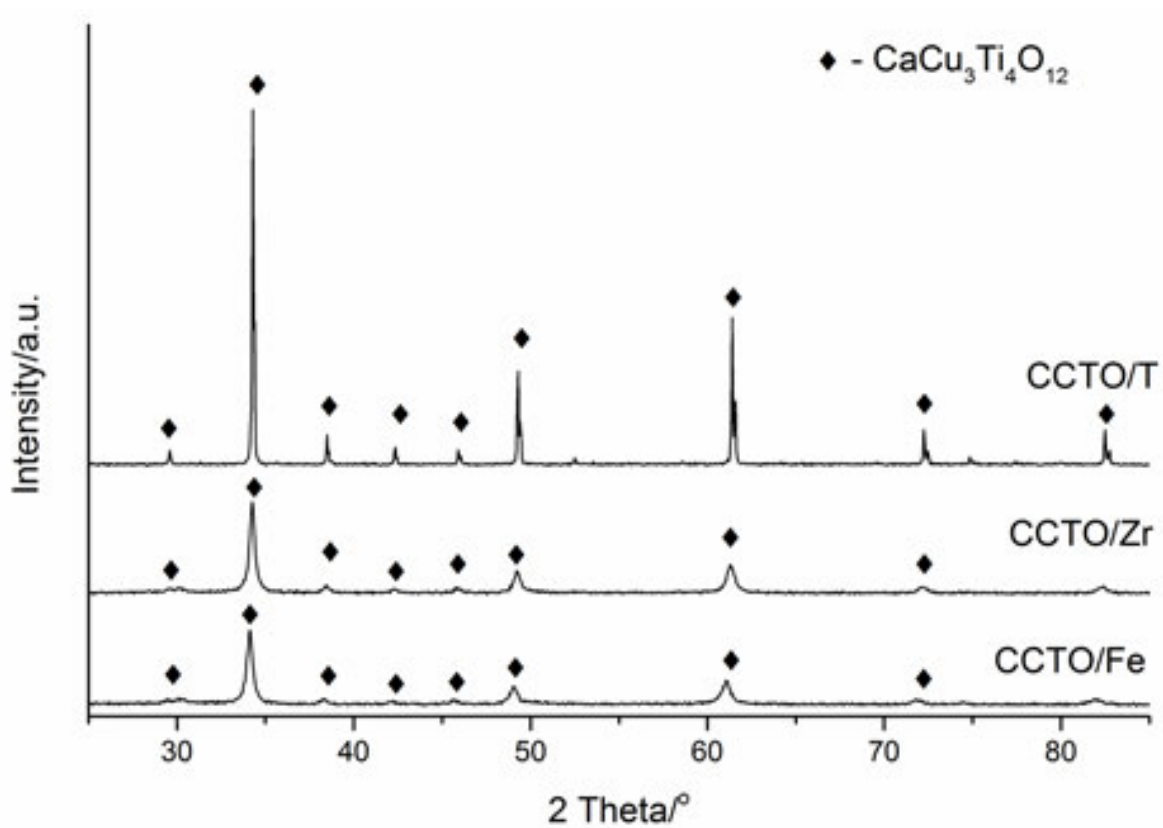
It is possible to postulate that the diffused character of the phase transition in  $\text{BaTiO}_3/\text{Zr}$  and  $\text{BaTiO}_3/\text{Fe}$  ceramics is caused by the presence of the impurities from the milling process.

#### b. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

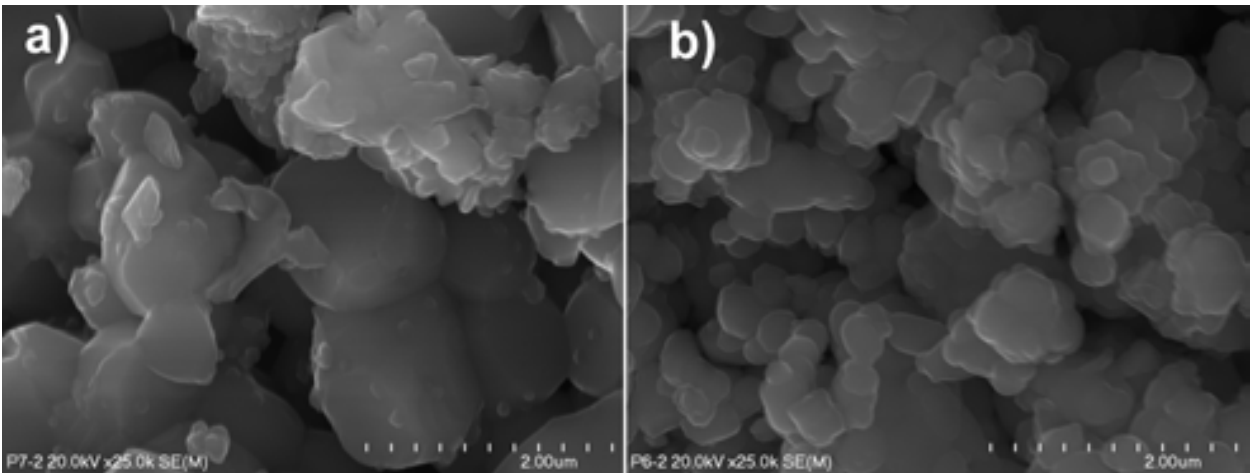
Figure 15 shows the XRD patterns for the mechanochemically synthesized  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO/Fe and CCTO/Zr, reactor and balls of steel, and  $\text{ZrO}_2$ , respectively) and by high-temperature treatment (CCTO/T). As can be seen, all samples are monophasic – CCTO. Syntheses details are given in Appendix A3.

Significant differences in the intensities and widths of diffraction reflexes of materials produced by high-temperature and mechanochemical route indicate different degrees of crystallinity and grain morphology. These observations were confirmed by SEM studies (Figure 16a, b).

High-temperature synthesis method results in grain growth (1.5–2.5  $\mu\text{m}$ ) and sintering of grains giving uneven distribution of particle size (Figure 16a). In addition, in material at the grain boundaries are visible places with high concentration of copper caused by the presence of sinters and a change in the oxidation state of copper ions during calcination at high temperature. This phenomenon is well known and this is the main problem during production of this material by methods where high-temperature processing is used. Such a ceramic is chemically inhomogeneous in volume of the particles and at their boundaries.  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  prepared mechanochemically is characterized by a uniform size distribution in the range of



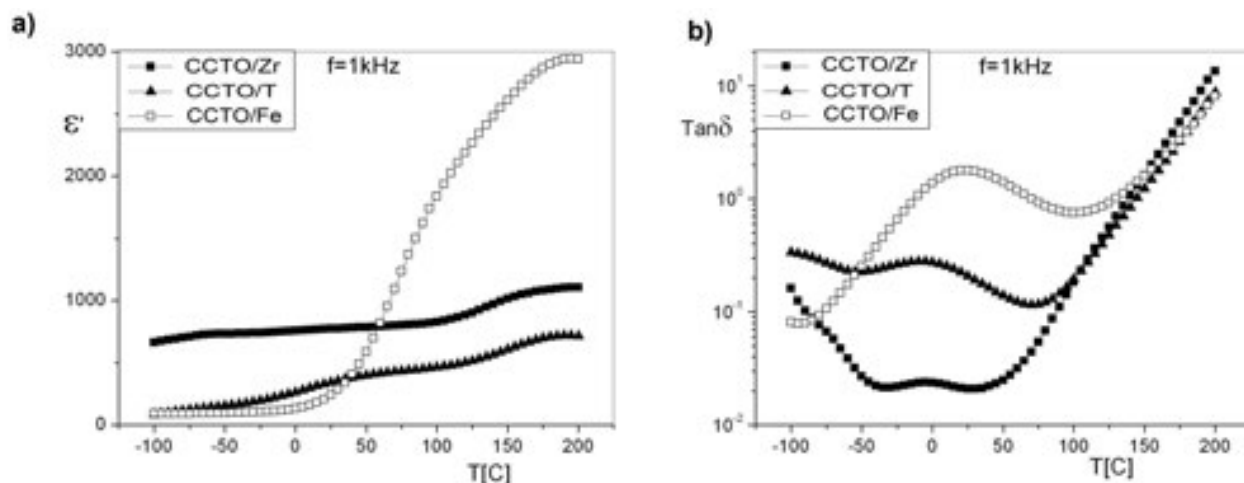
**Figure 15.** XRD patterns of mechanochemically synthesized  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO/Fe and CCTO/Zr, reactor and balls of steel and  $\text{ZrO}_2$ , respectively) and by high-temperature treatment (CCTO/T) [60]



**Figure 16.** SEM images of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  : (a) high-temperature treatment (CCTO/T), (b) mechanochemical synthesis (CCTO/Zr) [60]

100–500nm and the lack of the high-temperature processing during synthesis eliminates the problem of chemical inhomogeneity of the material (Figure 16b). Grain boundary problem in ceramics  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and their influence on its dielectric properties are widely discussed in the papers [62–65]. Dielectric properties of studied perovskite-related  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  compound

synthesized under different conditions as a temperature relationship of the real component of dielectric permittivity ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) at the field frequency of 1 kHz are presented in Figure 17a and b, respectively.



**Figure 17.** Temperature relationship of the real component of (a) dielectric permittivity ( $\epsilon'$ ) and (b) dielectric loss ( $\tan \delta$ ) at the field frequency of 1 kHz for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  synthesized under different conditions [60]

The presence of small amount of zirconia (CCTO/Zr) causes the smallest changes in the electric permittivity ( $\epsilon'$ ) versus temperature, similar to CCTO/T nature. From the practical point of view, such effect as well as very low and stable value of dielectric loss ( $\tan \delta$ ) in the temperature range of  $-50$ – $50^\circ\text{C}$  is very convenient. Material behaves differently with the presence of metallic iron (CCTO/Fe). From the ambient temperature, a significant increase in the value of  $\epsilon'$  is observed. At  $200^\circ\text{C}$ ,  $\epsilon'$  reaches a value of about 3,000. However, high values of dielectric loss ( $\tan \delta$ ), indicating the conversion of electrical energy into heat, disqualify this ceramics for practical applications, e.g., as capacitor material.

## 6. Summary

Mechanochemistry being one of the easiest and cheapest methods of producing nanomaterials also enables the synthesis of advanced ceramics with perovskite structure. It is an interesting alternative to other methods to produce such compounds. As is shown in the presented examples, the reactions between the substrates in the form of oxide are going exclusively by high-energy milling without requiring long-term calcination at high temperature. This helps to avoid many technological difficulties and problems related to powder morphology and properties. Using mechanochemical synthesis of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  eliminates problems associated with inhomogeneity of grains and intergranular boundaries. Consequently, the product prepared mechanochemically has much better functional properties than the same obtained by conventional high-temperature solid phase synthesis. The same is the case of the popular electroceramics PZT ( $\text{PbZr-TiO}_3$ ), due to the high volatility of lead at high temperature. Using

other synthesis techniques, it is difficult to maintain the stoichiometry of the compound. Applying for this purpose, the mechanochemical treatment not only omitted this problem but it is also able to produce nanometric ceramics.

In spite of the synthesis of perovskite compounds, mechanochemical technique can be applied also to modification of their properties. Selection of appropriate conditions for high-energy ball milling process is very important.

Thus, mechanochemistry realized by high-energy ball milling becomes recently the more environmentally acceptable for perovskite processing mainly for the following reasons:

- Simplify the synthesis process to one step
- Reduce the cost of chemicals and/or heat used in a traditional way
- Give the micro/nanosized products.

## 7. Appendix

### A1.

Mechanochemical treatment was provided using two different high-energy laboratory planetary mills with vial (250 ml) and balls (10 mm diameter) made of Ni-Cr steel:

1. *Pulverisette-6* (by Fritsch GmbH) with a rotation speed 500 rpm.
2. *Activator-2S* (by Activator Corp. Novosibirsk) a rotation speed 1,000 rpm.

The subsequent calcination processes of powders were carried out in Nabertherm HTC 03/15 laboratory furnace in air atmosphere.

### A2.

Mechanochemical treatment was provided using Fritsch *Pulverisette-6* planetary ball mill with vial (250 ml) and balls (10 mm diameter) made of ZrO<sub>2</sub>. Milling parameters: rpm = 500; ball to powder mass ratio: BPR = 20:1; milling time: 1.5 h; atmosphere: air.

Preparation of reference samples by high-temperature solid phase reaction. The reactants powders were ground together in a stoichiometric ratio in an agate mortar, pressed into pellet discs 4 mm thick and of 12 mm in diameter and sintered in air with the use of a Nabertherm HTC 03/15 laboratory furnace for 12 h at the temperature of 1,350°C.

### A3.

Mechanochemical treatment was provided using Fritsch *Pulverisette-6* planetary ball mill with vial (250 ml) and balls (10 mm diameter) made of ZrO<sub>2</sub> and steel. Milling parameters: rpm = 500; ball to powder mass ratio: BPR = 20:1; milling time: 1.5 h; atmosphere: air.

Preparation of reference samples by high-temperature solid phase reaction – as in the A2.

The phase identification and physicochemical characteristics of milling products were determined using the following methods:

- X-ray powder diffraction (XRD) patterns were recorded on a Philips
- X'Pert or Philips PW 1830 diffractometers (CuK $\alpha$ ).
- Morphology of the surface were observed using a the scanning electron microscope (SEM) HITACHI S-4700 instrument with X-ray EDS analysis and the Philips SEM 525.
- Specific surface area (BET) of samples was determined using Accelerated Surface Area and Porosimetry Analyzer (ASAP) 2020 from Micrometrics.
- The elemental compositions of the samples were measured by an energy-dispersive X-ray fluorescent spectroscopy (XRF) using a XRF Bruker S4 Explorer instrument.
- The dielectric spectroscopy measurements in the frequency domain were performed at frequency ranging from 20 Hz to 1 MHz with the use of an LCR Agilent 4284A meter and a Quatro Krio 4.0 temperature control system. The dielectric property measurements were carried out at temperature between 473 and 173 K with a 5 K step. To perform the dielectric measurements, the samples of 7 mm in diameter and 2.5 mm thick were covered with silver electrodes.

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## References

- [1] Setter N, Wasser R. Electroceramic materials. *Acta Mater* 2000;48(1):151–78. DOI: 10.1016/S1359-6454(99)00293-1
- [2] Waser R. Modeling of electroceramics – applications and prospects. *J Eur Ceramic Soc* 1999;19(6):655–64. DOI: 10.1016/S0955-2219(98)00293-3
- [3] Scott JF. Applications of modern ferroelectrics. *Science* 2007;315(5814):954–9. DOI: 10.1126/science.1129564
- [4] Eerestein W, Mathur ND, Scott JF. Multiferroic and magnetoelectric materials. *Nature* 2006;442(7104):759–65. DOI: 10.1038/nature05023
- [5] Nuraje N, Su K. Perovskite ferroelectric nanomaterials. *Nanoscale* 2013;5(19):8752–80. DOI: 10.1039/c3nr02543h
- [6] Cohen RE. Origin of ferroelectricity in perovskite oxides. *Nature* 1992;358(6382):136–8. DOI: 10.1038/358136a0
- [7] Li S, Eastman JA, Li Z, Foster CM, Newnham RE, Cross LE. Size effects in nanostructured ferroelectrics. *Phys Lett A: Gen Atom Solid State Phys* 1996;212(6):341–6. DOI: 10.1016/0375-9601(96)00077-1
- [8] Kretschmer R, Binder K. Surface effects on phase transitions in ferroelectrics and dipolar magnets. *Phys Rev B* 1979;20(3):1065–76. DOI: 10.1103/PhysRevB.20.1065
- [9] Cottam MG, Tilley DR, Zeks B. Theory of surface modes in ferroelectrics. *J Phys C: Solid State Phys* 1984;17(10):1793–823. DOI: 10.1088/0022-3719/17/10/022
- [10] Binder K. Surface effects on phase transitions in ferroelectrics and antiferroelectrics. *Ferroelectrics* 1981;35(1):99–104. DOI: 10.1080/00150198108017670
- [11] Liu J, Chen W, Wang B, Zheng Y. Theoretical methods of domain structures in ultra-thin ferroelectric films: a review. *Materials* 2014;6(9):6502–68. DOI: 10.3390/ma7096502
- [12] Haertling GH. Ferroelectric ceramics: history and technology. *J Am Ceramic Soc* 1999;82(4):797–818.
- [13] Somani V, Kalita SJ. Synthesis and characterization of nanocrystalline barium strontium titanate powder via sol-gel processing. *J Electroceramics* 2007;18(1):57–65. DOI: 10.1007/s10832-007-9008-7
- [14] Senna M. A straight way toward phase pure complex oxides. *J Eur Ceramic Soc* 2005;25(12):1977–84. DOI: 10.1016/j.jeurceramsoc.2005.03.002
- [15] Barboux P, Griesmar P, Ribot F, Mazerolles L. Homogeneity-related problems in solution derived powders. *J Solid State Chem* 1995;117(2):343–50. DOI: 10.1006/jssc.1995.1283

- [16] Bocquet JF, Chhor K, Pommier C. Barium titanate powders synthesis from solvothermal reaction and supercritical treatment. *Mater Chem Phys* 1999;57(3):272–80. DOI: 10.1016/S0254-0584(98)00233-8
- [17] Dutta PK, Asiaie R, Akbar SA, Zhu W. Hydrothermal synthesis and dielectric properties of tetragonal BaTiO<sub>3</sub>. *Chem Mater* 1994;6(9):1542–8. DOI: 10.1021/cm00045a011
- [18] Sengodan R, Chandar Shekar B. Characterization of barium strontium titanate (BST) single crystal nanorods prepared by wet chemical method. *Optoelectronics Adv Mater Rapid Commun* 2014;8(7):617–21.
- [19] Somani V, Kalita SJ. Synthesis and characterization of nanocrystalline barium strontium titanate powder via sol-gel processing. *J Electroceramics* 2007;18(1):57–65. DOI: 10.1007/s10832-007-9008-7
- [20] Kaur J, Kotnala RK, Verma KC. Surfactant free hydrothermal synthesis, electrical, optical and ferroelectric properties of BaTiO<sub>3</sub> nanoparticles. *J Optoelectronics Adv Mater* 2012;14(3):219–23.
- [21] Piotr D, Wojciech B, Wieczorek-Ciurowa K, Czeslaw K. Controlled mechanochemical synthesis and properties of a selected perovskite-type electroceramics. *Mater Sci Poland* 2013;31(3):462–70. DOI: 10.2478/s13536-013-0126-4
- [22] Zhang Q, Saito F. A review on mechanochemical syntheses of functional materials. *Adv Powder Technol* 2012;23(5):523–31. DOI: 10.1016/j.appt.2012.05.002
- [23] Wieczorek-Ciurowa K, Gamrat K. Mechanochemical syntheses as an example of green processes. *J Thermal Analysis Calorimetry* 2007;88(1):312–7. DOI: 10.1007/s10973-006-8098-9
- [24] Senna M. Solid state mechanochemical processes for better electroceramics. *Acta Chim Sloven* 2014;61(3):425–31.
- [25] Wongmaneerung R, Chaisan W, Khamman O, Yimnirun R, Ananta S. Potential of vibro-milling technique for preparation of electroceramic nanopowders. *Ceramics Int*. 2008;34(4):813–7. DOI: 10.1016/j.ceramint.2007.09.090
- [26] Murty BS, Ranganathan S. Novel materials synthesis by mechanical alloying/milling. *Int Mater Rev* 1998;43(3):101–41. DOI: 10.1179/095066098790105654
- [27] Baláž P, Baláž M, Bujňáková Z. Mechanochemistry in technology: from minerals to nanomaterials and drugs. *Chem Eng Technol* 2014;37(5):747–56. DOI: 10.1002/ceat.201300669
- [28] Wieczorek-Ciurowa K, Dulian P, Bak W, Kajtoch C. High-energy ball milling as a green chemistry method for modification of CaTiO<sub>3</sub> electrical properties. *Przemysl Chem* 2011;90(7):1400–3.

- [29] Venkataraman KS, Narayanan KS. Energetics of collision between grinding media in ball mills and mechanochemical effects. *Powder Technol* 1998;96(3):190–201. DOI: 10.1016/S0032-5910(97)03368-8
- [30] Menyhart M, Miskiewicz L. Communiton and structural changes in a jet mill. *Powder Technol* 1976;15(2):261–6. DOI: 10.1016/0032-5910(76)80055-1
- [31] Baláž P, Achimovičová M, Baláž M, Billik P, Cherkezova-Zheleva Z, Criado JM, Delogu F, Dutková E, Gaffet E, Gotor FJ, Kumar R, Mitov I, Rojac T, Senna M, Streletskii A, Wieczorek-Ciurowa K. Hallmarks of mechanochemistry: from nanoparticles to technology. *Chem Soc Rev* 2013;42(18):7571–637. DOI: 10.1039/c3cs35468g
- [32] Erdemolu M, Baláž P. An overview of surface analysis techniques for characterization of mechanically activated minerals. *Mineral Process Extract Metallurgy Rev* 2012;33(1):65–88. DOI: 10.1080/08827508.2010.542582
- [33] Beyer MK, Clausen-Schaumann H. Mechanochemistry: The mechanical activation of covalent bonds. *Chem Rev* 2005;105(8):2921–48. DOI: 10.1021/cr030697h
- [34] James SL, Adams CJ, Bolm C, Braga D, Collier P, Friiç T, Grepioni F, Harris KDM, Hyett G, Jones W, Krebs A, MacK J, Maini L, Orpen AG, Parkin IP, Shearouse WC, Steed JW, Waddell DC. Mechanochemistry: opportunities for new and cleaner synthesis. *Chem Soc Rev* 2012;41(1):413–47. DOI: 10.1039/c1cs15171a
- [35] Boldyreva E. Mechanochemistry of inorganic and organic systems: what is similar, what is different? *Chem Soc Rev* 2013;42(18):7719–38. DOI: 10.1039/c3cs60052a
- [36] Suryanarayana C. Mechanical alloying and milling. *Prog Mater Sci* 2001;46(1):1–184. DOI: 10.1016/S0079-6425(99)00010-9
- [37] Ivanov E, Suryanarayana C. Materials and process design through mechanochemical routes. *J Mater Syn Process* 2000;8(3):235–44. DOI: 10.1023/A:1011372312172
- [38] Sopicka-Lizer M, editor. High-energy ball milling: mechanochemical processing of nanopowders. 1st Editionst ed. Woodhead Publishing Limited; 2010. 440 p. DOI: 10.1533/9781845699444
- [39] Rumpf H. Physical aspects of communiton and new formulation of a law of communiton. *Powder Technol* 1973;7(3):145–59. DOI: 10.1016/0032-5910(73)80021-X
- [40] Wieczorek-Ciurowa K, Dulian P, Nosal A, Domagała J. Effects of reagents' nature on mechanochemical synthesis of calcium titanate. *J Thermal Analysis Calorimetry* 2010;101(2):471–7. DOI: 10.1007/s10973-010-0802-0
- [41] Boldyrev VV. Mechanochemistry and mechanical activation of solids. *Solid State Ionics* 1993;63–65(C):537–43. DOI: 10.1016/0167-2738(93)90157-X
- [42] Hainovsky NG, Pavlyukhin YuT, Boldyrev VV. Application of mechanical activation to the synthesis of high temperature superconductors. *Mater Sci Eng B* 1991;8(4):283–6. DOI: 10.1016/0921-5107(91)90048-Z

- [43] Koch CC. The synthesis and structure of nanocrystalline materials produced by mechanical attrition: a review. *Nanostructured Mater* 1993;2(2):109–29. DOI: 10.1016/0965-9773(93)90016-5
- [44] Wieczorek-Ciurowa K, Rakoczy J, Błońska-Tabero A, Filipek E, Nizioł J, Dulian P. Mechanochemical synthesis of double vanadate in Cu-Fe-V-O system and its physicochemical and catalytic properties. *Catalys Today* 2011;176(1):314–7. DOI: 10.1016/j.cattod.2010.12.007
- [45] Wieczorek-Ciurowa K. Illustration of selected functional inorganic materials fabricated by mechanochemical approaches. *Acta Phys Polon A* 2014;126(4):1049–52. DOI: 10.12693/APhysPolA.126.1049
- [46] Wieczorek-Ciurowa K, Gamrat K. Some aspects of mechanochemical reactions. *Mater Sci Poland* 2007;25(1):219–32.
- [47] Rougier A, Soiron S, Haihal I, Aymard L, Taouk B, Tarascon J-M. Influence of grinding on the catalytic properties of oxides. *Powder Technol* 2002;128(2):139–47. DOI: 10.1016/S0032-5910(02)00191-2
- [48] Ullah M, Ali ME, Hamid SBA. Surfactant-assisted ball milling: a novel route to novel materials with controlled nanostructure: a review. *Rev Adv Mater Sci* 2014;37(1):1–14.
- [49] Janot R, Guérard D. Ball-milling in liquid media: applications to the preparation of anodic materials for lithium-ion batteries. *Prog Mater Sci* 2005;50(1):1–92. DOI: 10.1016/S0079-6425(03)00050-1
- [50] Balogh J, Bujdosó L, Kaptás D, Kemény T, Vincze. The role of impurities in the crystallization of ball-milled amorphous alloys. *Mater Sci Forum* 1998;269(1):63–8.
- [51] Courtney TH, Maurice D. Process modeling of the mechanics of mechanical alloying. *Scripta Materialia* 1996;34(1):5–11. DOI: 10.1016/1359-6462(95)00464-5
- [52] Gotor FJ, Achimovicova M, Real C, Balaz P. Influence of the milling parameters on the mechanical work intensity in planetary mills. *Powder Technol* 2013;233:1–7. DOI: 10.1016/j.powtec.2012.08.031
- [53] Wieczorek-Ciurowa K, Gamrat K, Shirokov Ju G. Mechanism of mechanochemical reactions in malachite-active metal systems. *Thermochim Acta* 2003;400(1):221–5. DOI: 10.1016/S0040-6031(02)00495-1
- [54] Takacs L. Self-sustaining reactions induced by ball milling. *Prog Mater Sci* 2002;47(4):355–414. DOI: 10.1016/S0079-6425(01)00002-0
- [55] Wieczorek-Ciurowa K, Gamrat K, Paryło M, Shirokov Ju G. The influence of aluminium and aluminium oxide on the effects of mechanical activation of nickel hydroxycarbonate. *J Thermal Analys Calorimetry* 2002;69(1):237–45. DOI: 10.1023/A:1019958328002

- [56] Avvakumov EG, Karakchiev LG, Gusev AA, Vinokurova OB. Preparation of disperse ceramic materials by soft mechanochemical synthesis. *Mater Sci Forum* 2002;386:245–50.
- [57] Bak W, Dulian P, Sitko D, Garbarz-Glos B, Kajtoch C, Wieczorek-Ciurowa K, Smeltere I. Effect of variable valence ion doping on the dielectric properties of BaTiO<sub>3</sub>-based materials. *Ferroelectrics* 2014;464(1):35–41. DOI: 10.1080/00150193.2014.892810
- [58] Dulian P, Bak W, Wieczorek-Ciurowa K, Kajtoch C. Dielectric properties of vanadium doped barium titanate synthesized via high-energy ball milling. *Mater Sci Poland* 2014;32(2):257–63. DOI: 10.2478/S13536-013-0185-6
- [59] Dulian P, Bak WB, Wieczorek-Ciurowa K, Kajtoch C. Dielectric behaviour of BaTiO<sub>3</sub>-SrTiO<sub>3</sub> solid solutions fabricated by high-energy ball milling. *Key Eng Mater* 2014;605:63–66. DOI: 10.4028/www.scientific.net/KEM.605.63
- [60] Dulian P, Bak W, Wieczorek-Ciurowa K, Kajtoch C. Comparative studies of dielectric properties of Ca<sub>0.25</sub>Cu<sub>0.75</sub>TiO<sub>3</sub> ceramics produced by mechanochemical synthesis and in the way of high-temperature treatment. *Key Eng Mater* 2013;543:326–9. DOI: 10.4028/www.scientific.net/KEM.543.326
- [61] Bak W, Dulian P, Grabarz-Glos B, Kajtoch Cz, Wieczorek-Ciurowa K. Dielectric behaviour of (Ba<sub>1-x</sub>Nax)(Ti<sub>1-x</sub>Nbx)O<sub>3</sub> ceramics obtained by conventional and mechanochemical synthesis. *Ferroelectrics*. Forthcoming.
- [62] Dulian P, Bak W, Kajtoch Cz, Wieczorek-Ciurowa K. A high-energy ball milling as a useful technique for the synthesis of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> electroceramics. *Acta Phys Polon A* 2014;126(4):931–7. DOI: 10.12693/APhysPolA.126.931
- [63] Lunkenheimer P, Fichtl R, Ebbinghaus SG, Loidl A. Nonintrinsic origin of the colossal dielectric constants in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. *Phys Rev B Condens Matter Mater Phys* 2004;70(17):1–4. DOI: 10.1103/PhysRevB.70.172102
- [64] Adams TB, Sinclair DC, West AR. Giant barrier layer capacitance effects in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> ceramics. *Adv Mater* 2002;14(18):1321–3. DOI: 10.1002/1521-4095(20020916)14:18<1321::AID-ADMA1321>3.0.CO;2-P
- [65] Bender BA, Pan M-J. The effect of processing on the giant dielectric properties of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. *Mater Sci Eng B: Solid-State Mater Adv Technol* 2005;117(3):339–47. DOI: 10.1016/j.mseb.2004.11.019