# Phase transformations kinetics in barium titanate synthesis by mechanochemical processing

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*Abstract*

This article presents the research results on a dry mechanochemical synthesis of barium titanate at a low temperature in which the reaction model and kinetics were determined during the activation of a powder mixture of titanium dioxide and barium oxide. The solid-state reaction achieved high degree of conversion (0.99). Successive analyses were conducted throughout the reaction, revealing the presence of both the starting powders and newly formed intermediate compounds. Phase transformations were monitored via X-ray diffraction, allowing the dynamics of the synthesis to be characterized. It was established that, for the given system, 440 min of mechanical activation in a high-energy vibration mill was required to complete the neutralization reaction and produce barium titanate. The reaction mixture composition was tracked by sampling at five intervals, confirming the presence of intermediate compounds and mapping the reaction pathway from the initial barium and titanium oxides to the final $BaTiO_3$ product.

*Keywords:* Solid-state reaction; BaO; $TiO_2$; reaction mechanism; kinetics; mechanochemical synthesis.

## 1. INTRODUCTION

Barium titanate is a material that has long been of great interest due to its properties. It is a very stable (mechanically and chemically) material with ferroelectric properties that is easy to prepare. It has found application in capacitors, superconductors, piezoelectric devices and PTC thermistors thanks to its high dielectric constant and low loss characteristics [1].

However, dielectric properties of barium titanate nanoparticles are greatly influenced by the applied synthesis method. There are several methods for the synthesis of barium titanate: hydrothermal, microwave-assisted hydrothermal, electrochemical, polymer precursor (Pechini) and the dry process synthesis, *i.e.* mechanochemical synthesis [2]. The aim of the latter studies was not to improve the dielectric properties of barium titanate, but to examine the possibility of obtaining it by a dry mechanochemical process and to monitor the kinetics of this process, which is continued in the present work.

Solid-state reactions have long captured the interest of researchers, particularly when these processes offer advantages such as simpler synthesis methods and reduced energy consumption compared to equivalent liquid-phase reactions. In recent years, mechanochemical synthesis has gained prominence in the production of various compounds. Understanding the specific parameters characteristic of solid-state matter is crucial for this type of research [3]. In addition to their advantages, solid-state reactions also have disadvantages that can make them challenging for certain applications [4] such as the often requirement for high temperatures (above 700 °C), presenting an additional economic investment in the desired process. Also, due to the necessary diffusion of reactants in the solid phase, the process rate

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is lower than in liquid-phase reactions. Due to the nature of the process, it is difficult to control the morphology of the product and formation of new, secondary phases due to incomplete reactions and diffusion limited processes. Another problem is the presence of mechanically hard, strongly bonded agglomerates at high processing temperatures, which are difficult to disintegrate. In contrast to solid-state reactions, in reactions that take place in sol-gel systems, better control of the final product in terms of homogeneity, stoichiometry and purity is possible.

Unlike liquid-phase reactions, where particles exhibit greater mobility due to the presence of ions in a fluid medium, solid-state reactions require direct contact between the initial components, which have not decomposed into ions. Not all reactions that occur in the liquid phase can be replicated in the solid phase. For such reactions to be feasible, they must be thermodynamically favourable, meaning that the activation energy necessary to initiate the chemical reaction must be adequately supplied. The energy input to the system has to meet or exceed the activation energy required for the reaction to proceed in the solid state [5-8].

When the starting components are ground in their solid state, bringing the particles into contact without dissociation and a chemical reaction occurring with sufficient energy input, the process is referred to as mechanochemical synthesis, which typically occurs in a reactor. These reactions differ from classic acid-base neutralization reactions. However, if the product of a mechanochemical reaction is salt formed from a base and an acid, with the initial components being a base anhydride and an acid anhydride, the reaction can still be categorized as a neutralization reaction. This reaction occurs due to the collision of mechanically activated particles, coupled with the sufficient energy input that leads to dissociation. The system becomes excited, the crystal lattice is disrupted, and new bonds are formed between particles. The presence of broken bonds and excited electrons, which act as carriers for the formation of new bonds, drives the reaction forward. In this context, only the Lewis definitions of acid-base reactions apply [9,10]. Bases serve as electron donors, while acids are electron acceptors under the newly established conditions of the mechanochemical neutralization reaction. The most significant factor influencing such complex reactions is the input of mechanical energy, which determines the reaction time necessary to achieve a complete reaction in the solid phase [11]. When titanium dioxide and barium oxide are the initial components in such a system, it is possible to synthesize barium titanate as the final product [12-17].

A mechanochemical process for obtaining barium bismuth titanate was described, whereby the synthesis was carried out in a planetary ball mill in air atmosphere followed by a comprehensive analysis of the resulting product [12]. Also, mechanochemical activation of a stoichiometric powder mixture $2Bi_2O_3{\cdot}3TiO_2$ was performed to obtain $Bi_4Ti_3O_{12}$ [13]. X-ray powder diffraction was used to monitor the intermediate as well as the final product, and the results were used to establish the kinetics of the process. In another study mechanochemical activation of a $2Bi_2O_3{\cdot}3TiO_2$ mixture was performed in a planetary ball mill and the crystallite size, amount of the amorphous phase and the transformed fraction were monitored using the X-ray diffraction analysis method. The authors established that there was deformation of the crystal lattice and destruction of the structure of the starting material [14]. Also, after a certain amount of grinding time, a very disordered, amorphous/nanocrystalline structure was obtained. There are some other papers describing synthesis of $BaTIO_3$ by solid-state synthesis methods with lower energy of activation of the initial samples; those methods produced poorly uniform $BaTiO_3$ at higher temperatures, with intermediate phases such as $Ba_2TiO_4$ or $BaTi_2O_5$ [18-20].However, in one study it was indicated that $BaTiO_3$ can be obtained at lower temperatures in contrast to results previously reported in the literature [21].

To comprehend this synthesis process fully, it is essential to identify intermediate compounds and monitor both the reaction mechanism and kinetics [22-28]. The aim of this research was to derive the reaction mechanism and investigate the kinetics of barium titanate synthesis via mechanochemical activation in a vibrating mill with rings.

## 2. EXPERIMENTAL

Mechanochemical neutralization reactions involving barium oxide (BaO) and titanium dioxide ($TiO_2$) were conducted using a high-energy vibration mill with torsion springs and annular working elements, manufactured by KHD Humboldt Wedag A.G., Germany (model MH954/3). The mill comprises a base and a horizontally positioned shutter. The working vessel is a cylindrical container made of stainless steel, with a depth of 40 mm and an internal diameter of 170 mm. The working elements consist of two freely moving concentric rings, also made of stainless steel, with a total weight of 3 kg.

The grinding process lasted for 440 min, with a motor power of 0.8 kW, the energy input to the system equivalent to a grinding disc speed of 800 rpm.

Atomic absorption spectrophotometry (AAS) was selected as a precise and reliable method for monitoring the reaction kinetics, and based on literature data and blank tests, 10% acetic acid was chosen as the most suitable solvent. Chemical analysis was carried out using a Perkin Elmer Analyst 703 (USA) atomic absorption spectrophotometer. The concentrations of unreacted $Ba^{2+}$ ($\lambda$ = 553.6 nm) and $Ti^{4+}$ ($\lambda$ = 364.3 nm) ions were determined in the reaction mixture at specific time intervals, after dissolving the samples in this solvent. In this solution, only the oxide of the corresponding metal dissolves, forming acetate, while titanium dioxide and possibly synthesized titanate remain undissolved as a product of the reaction. The measurement uncertainty was 0.49 %. Practically, kinetic diagrams of the mechanochemical neutralization reactions were determined as follows: during the experiment, samples of the system in the amount of 0.1 g (analytical balance AE 165 MX 104 (Mettler, Switzerland) were taken at certain time intervals. The samples were dissolved in 250 ml of 10 % acetic acid solution. After filtering the suspension in the clear solution, the content of the appropriate alkaline metal ($Ba^{2+}$) and titanium was determined by using an AAS. Based on the obtained results, the degree of synthesis of the appropriate sample was calculated. From a set of calculations for the time series of mechanochemical synthesis, a kinetic diagram for the corresponding mechanochemical reactions was constructed.

The identification of crystalline phases formed during the solid-state reaction was carried out using X-ray powder diffraction (XRD). The samples were recorded and analysed using an automated diffractometer PW-1710 (Philips, Netherlands) equipped with a copper tube, operating at 40 kV and 35 mA. The device features a graphite monochromator and a proportional counter filled with xenon gas. The scanning angle ($2\theta$) ranged from 4 to 65° with step of 0.02° and holding time 0.5 s. Phase identification was achieved by comparing the results with standard patterns from the JCPDS database. The XRD analysis enabled the determination of the types and quantities of crystalline phases present. Detection limit was below 2 % [29].

For these experiments, barium oxide (BaO *p.a.*, Fluka, Switzerland) was used as the basic reactant, and titanium dioxide ($TiO_2$ *p.a.*, Merck, Germany) as the acidic reactant. No specific preconditions regarding the crystal structure or particle size distribution of the starting components were imposed. The used mechanochemical reactor was designed for an optimal batch size of 50 to 150 g. In this study, 0.5 mol (76.7 g) of BaO and 0.5 mol (39.9 g) of $TiO_2$, giving a total of 116.6 g as calculated from the stoichiometric Equation (1), were used, which is within the optimal range.

$$BaO_{(s)} + TiO_{2(s)} = BaTiO_{3(s)}(Ba0\cdot TiO_2) \quad (1)$$

To identify the crystal structure of BaO, a qualitative XRD analysis was performed, as shown in Table 1 (*d*-interplanar spacing, $2\theta$ - diffraction angle) and Figure 1.

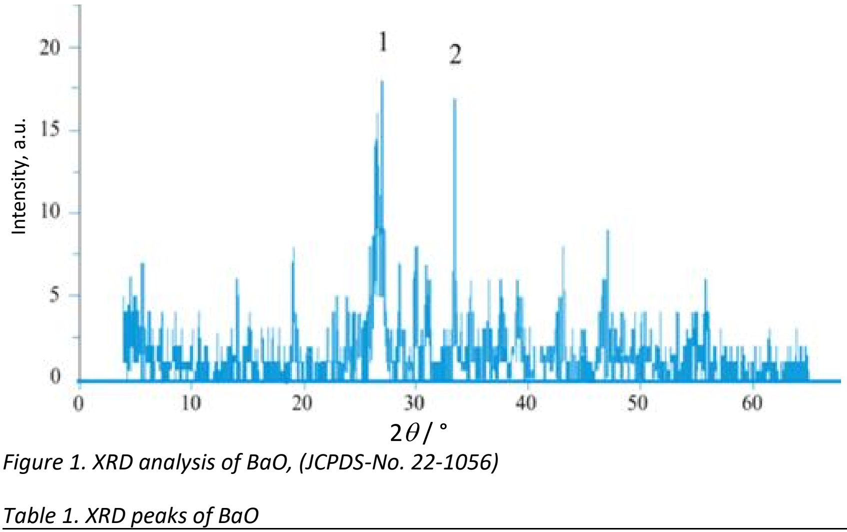

*Figure 1. XRD analysis of BaO, (JCPDS-No. 22-1056)*

*Table 1. XRD peaks of BaO*

| Peak (from Fig. 1) | *d* / nm | $2\theta$ / ° |
|---|---|---|
| 1 | 0.32895 | 27.085 |
| 2 | 0.26771 | 33.445 |

Analysing the X-ray diffraction (XRD) pattern in Figure 1 confirmed the presence of a significant amount of amorphous material. The diffraction peaks (d-values 3.2895 and 2.6771) indicate that the analysed sample corresponds to (poorly crystallized) barium oxide (BaO), (JCPDS-No. 22-1056). The XRD pattern of the starting titanium dioxide and its characteristic diffraction peaks are provided in Table 2 and Figure 2.

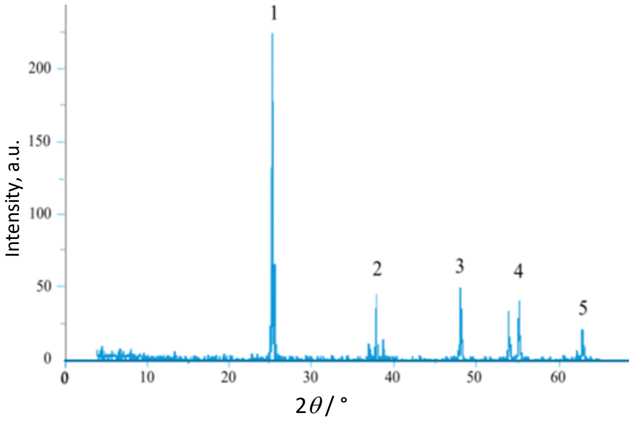

*Figure 2. XRD analysis of $TiO_2$, (JCPDS card No. 21-1272)*

*Table 2. XRD peaks of $TiO_2$*

| Peak (from Fig. 2) | *d* / nm | 2*θ* / ° |
|---|---|---|
| 1 | 0.35133 | 25.330 |
| 2 | 0.23778 | 37.805 |
| 3 | 0.18926 | 48.035 |
| 4 | 0.16667 | 55.055 |
| 5 | 0.14806 | 62.700 |

Throughout 440 min required for the complete synthesis of barium titanate via the mechanochemical process, samples were taken five times (at 30, 110, 200, 290, and 440 min) and each was analysed using XRD. The atomic absorption spectrophotometric (AAS) method was employed to analyse the chemical composition of the system corresponding to the activation time.

Based on the chemical analysis results, the degree of synthesis *S* [30], was calculated using Equation (2):

$$S = \left( 1 - \frac{0.25\left(m - bm_{\mathrm{Ti}}\right)}{m_0 a} \right) 100 \tag{2}$$

where $m_{\mathrm{Ti}}$ / g $L^{-1}$ is the mass concentration of titanium in the solution, $m$ / g $L^{-1}$ is the concentration of barium in solution, $m_0$ / g $L^{-1}$ is the mass concentration of the initial sample, $a$ denotes the mass fraction of barium in the initial sample with the value of 0.5885, $b$ represents the equivalence factor for barium's participation in the assumed intermediate compound of stoichiometric composition $BaTiO_3$, with $b$ = 2.8604 for the tested reaction system (BaO + $TiO_2$). The fundamental chemical-thermodynamic data, along with the corresponding equilibrium constant for the neutralization reaction between BaO and $TiO_2$, are as follows [31]: $\Delta H_r$ = -161.5 kJ $mol^{-1}$, $\Delta S^{\circ}_r$ = -12.69 J $mol^{-1}$, $\Delta G^{\circ}_r$ = -157.8 kJ $mol^{-1}$, $K_r = 1.31\times10^{28}$.

All data refer to a temperature of 20 °C: $\Delta H^{\circ}_r$ (change in the enthalpy of the reaction), $\Delta S^{\circ}_r$ (change in the entropy of the reaction), $\Delta G^{\circ}_r$ (change in the Gibbs free energy of the reaction), and $K_r$ (equilibrium constant of the reaction). All experiments were performed in triplicate.

## 3. RESULTS AND DISCUSSION

In our research, we also used X-ray structural analysis to monitor the results of activation and final synthesis as a function of activation time. To monitor dynamics of the formation of a new phase (*i.e.* the reaction product), samples of the reaction mixture were taken at specific time intervals (30 to 440 min) throughout the experiments, followed by qualitative XRD analyses. This approach allowed for the identification and monitoring of both the initial components and the products of the mechanochemical neutralization reactions. The XRD analysis of the sample after 30 min of mechanochemical activation was shown in a previous study [32]. The results demonstrated that high-energy milling induced significant changes in the crystal structure of the starting components, with trace amounts of barium titanate being detected.

The next sample was taken from the reaction system after 110 min of mechanochemical treatment. The XRD analysis of this sample is presented in Table 3 and Figure 3.

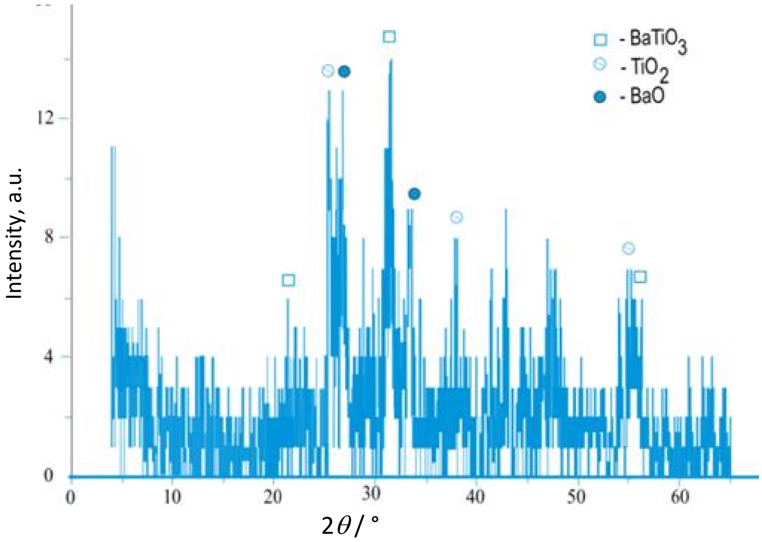

*Figure 3. XRD analysis of the reaction system ($BaO+TiO_2$) after 110 min of the mechanochemical treatment*

*Table 3. XRD peaks of the reaction system ($BaO+TiO_2$) after 110 min of the treatment (8 peaks registered)*

| Peak (from Fig. 3) | Assigned phase | *d* / nm | $2\theta$ / ° |
|---|---|---|---|
| 1-□ | $BaTiO_3$ | 0.39852 | 22.29 |
| 2-○ | $TiO_2$ | 0.35093 | 25.36 |
| 3-● | BaO | 0.33142 | 26.88 |
| 4-□ | $BaTiO_3$ | 0.28480 | 31.38 |
| 5-● | BaO | 0.26873 | 33.31 |
| 6-□ | $BaTiO_3$ | 0.23432 | 38.38 |
| 7-□ | $BaTiO_3$ | 0.16541 | 55.51 |
| 8-○ | $TiO_2$ | 0.16060 | 57.32 |

XRD peaks of the investigated system after 200 min of mechanochemical treatment are given in Table 4. As illustrated in Figure 4, the crystalline structure of the reaction system continues to degrade, bringing the entire reaction mixture to an almost entirely amorphous state.

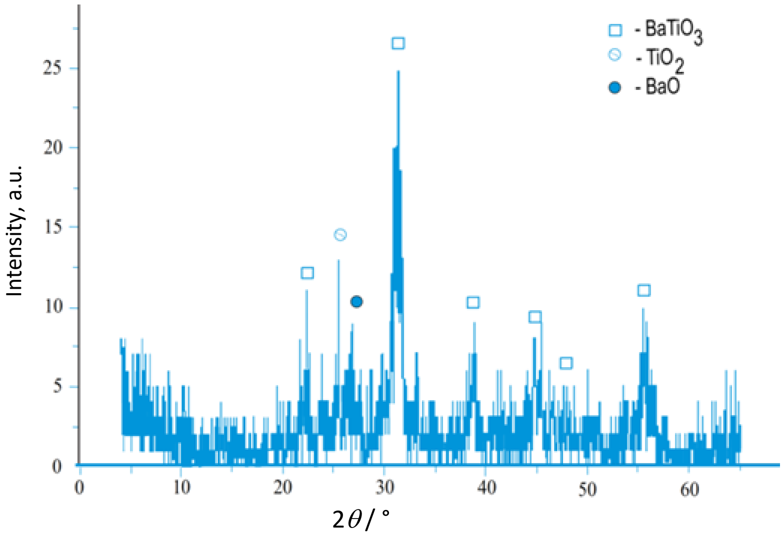

*Figure 4. XRD analysis of the reaction system ($BaO+TiO_2$) after 200 min of the mechanochemical treatment*

*Table 4. XRD peaks of the reaction system ($BaO+TiO_2$) after 200 min of the treatment (8 peaks registered)*

| Peak (from Fig. 4) | Assigned phase | *d* / nm | 2$\theta$ / ° |
|---|---|---|---|
| 1-□ | $BaTiO_3$ | 0.40145 | 22.12 |
| 2-○ | $TiO_2$ | 0.35031 | 25.40 |
| 3-● | BaO | 0.33105 | 26.91 |
| 4-□ | $BaTiO_3$ | 0.28295 | 31.59 |
| 5-□ | $BaTiO_3$ | 0.23196 | 38.79 |
| 6-□ | $BaTiO_3$ | 0.20133 | 44.99 |
| 7-□ | $BaTiO_3$ | 0.19235 | 47.21 |
| 8-□ | $BaTiO_3$ | 0.16588 | 55.34 |

Despite this, the detected peaks still indicate the presence of the starting reactants, barium oxide and titanium dioxide. It is noteworthy that the number of peaks associated with noise has significantly decreased, which clearly indicates a dynamic restructuring of the reaction system. The presence of an amorphous state in the system does not necessarily contradict previous observations; it may simply represent an intermediate phase in the reaction process leading to the formation of the final product's structure. Secondary phases such as $BaTi_2O_5$, $Ba_2TiO_4$ were not found, they are either absent or below the detection limit of the methods used. The subsequent XRD analysis was conducted on a sample taken from the reaction system after 200 min of mechanochemical activation.

The processes observed in the XRD analysis of the sample treated for 110 min continue and become even more pronounced. The main peak of barium titanate (*d*-value 2.8295) shows a noticeable increase in intensity, and all six characteristic peaks for barium titanate are clearly detected. The characteristic peaks of the reactants have largely disappeared, and the number of peaks associated with noise has further decreased. This indicates that after 200 min of mechanochemical treatment, a new phase- barium titanate-has clearly formed and dominates the reaction system. The increasing intensity of the characteristic peaks suggests the development and ordering of the crystal structure of the newly formed compound.

Table 5 and Figure 5 show the XRD analysis of the sample that underwent mechanochemical treatment for 290 min.

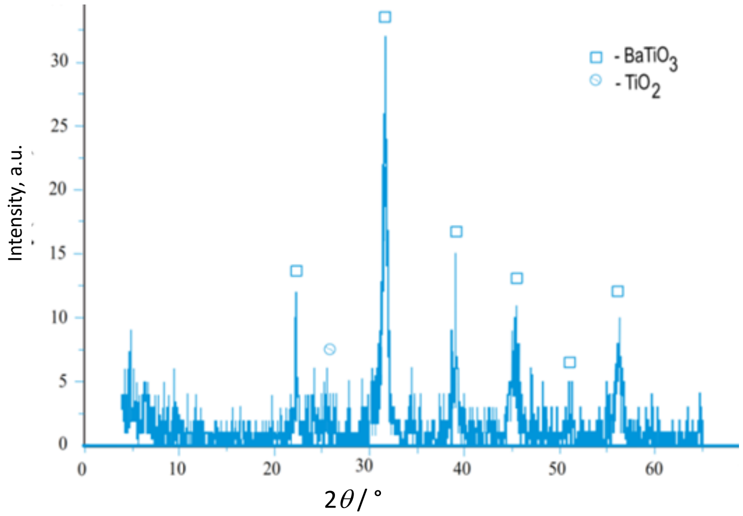

*Figure 5. XRD analysis of the reaction system ($BaO+TiO_2$) after 290 min of the mechanochemical treatment*

*Table 5. XRD peaks of the reaction system ($BaO+TiO_2$) after 290 min of the treatment (7 peaks registered)*

| Peak (from Fig. 5) | Assigned phase | *d* ( *nm* | 2$\theta$ / ° |
|---|---|---|---|
| 1-□ | $BaTiO_3$ | 0.39887 | 22.27 |
| 2-○ | $TiO_2$ | 0.34910 | 25.49 |
| 3-□ | $BaTiO_3$ | 0.28208 | 31.69 |
| 4-□ | $BaTiO_3$ | 0.23017 | 39.10 |
| 5-□ | $BaTiO_3$ | 0.20038 | 45.21 |
| 6-□ | $BaTiO_3$ | 0.19306 | 47.03 |
| 7-□ | $BaTiO_3$ | 0.16322 | 56.32 |

At this time, a well-defined crystal structure of the mechanochemical reaction product, barium titanate, had formed from the starting oxides BaO and $TiO_2$. Traces of the starting reactants were only observed in a remaining peak corresponding to titanium dioxide, while the increased number of peaks associated with the noise domain suggests that the mechanochemical synthesis of barium titanate was not yet complete. Chemical analyses confirming the absence of one of the reactants (barium oxide), along with the fact that the mechanochemical reaction was conducted with a stoichiometric ratio of reactants (as per Equation (1)), are reliable indicators that the mechanochemical neutralization reaction between the acid anhydride ($TiO_2$) and the oxide base hydroxide (BaO) was fully realized.

Figure 6 and Table 6 display the XRD analysis of the reaction product (Equation (1)) obtained from the mechanochemical reaction of BaO and $TiO_2$ after 440 min of treatment. Chemical analysis determined that the sample contained only 1.3 % of the starting barium oxide compared to the initial amount, indicating that 440 min represents the duration required for complete synthesis, considering the detection limit of the methods.

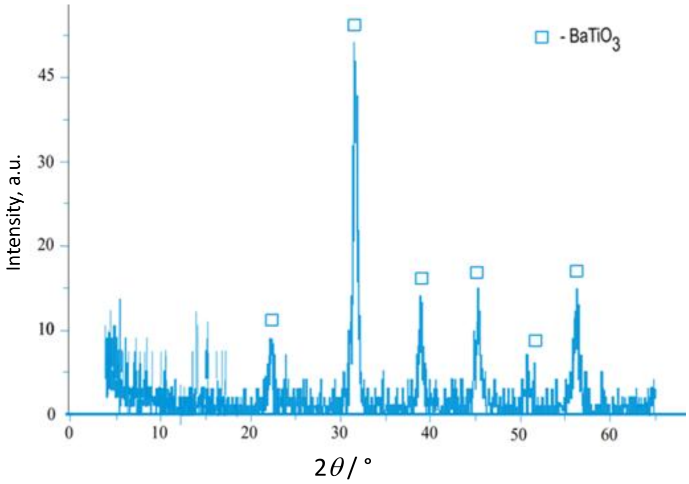

*Figure 6. XRD analysis of the reaction system ($BaO+TiO_2$) after 440 min of the mechanochemical treatment*

*Table 6. XRD peaks of the reaction system ($BaO+TiO_2$) after 440 min of the treatment*

| Peak (from Fig. 6) | Assigned phase | *d* / nm | $2\theta$ / ° |
|---|---|---|---|
| 1-□ | $BaTiO_3$ | 0.39905 | 22.26 |
| 2-□ | $BaTiO_3$ | 0.28217 | 31.68 |
| 3-□ | $BaTiO_3$ | 0.23128 | 38.91 |
| 4-□ | $BaTiO_3$ | 0.19936 | 45.46 |
| 5-□ | $BaTiO_3$ | 0.17929 | 50.89 |
| 6-□ | $BaTiO_3$ | 0.16343 | 56.24 |

Analysis of the diffraction maxima (Figure 6) revealed that the peak intensities correspond to the crystalline phases of barium titanate ($BaTiO_3$, *i.e* $BaO·TiO_2$). This suggests that after 440 min of mechanochemical treatment, the reaction described in Equation (1), has essentially reached completion, considering the detection limit of methods. The well-defined diffraction peaks of barium titanate, along with the absence of peaks corresponding to the starting reactants—barium oxide and titanium dioxide - could indicate the successful completion of the mechanochemical synthesis of barium titanate. Considering that the vibrating mill we used in researching the possibility of mechanochemical synthesis of barium titanate, at the end of the activation it was determined by X-ray structural analysis that the product is almost completely obtained in a stable crystalline state with the chemical formula $BaTiO_3$.

A detailed analysis of the diagrams presented in Figures 1 to 6 provides valuable insights into the mechanochemical synthesis of barium titanate ($BaTiO_3$). By analysing the progression of the crystal structures and recognizability of the peaks, the entire process can be divided into three experimental stages based on XRD and AAS analyses:

1. First stage (up to 30 min): During this initial phase, the crystal structure of the reaction system collapses significantly. It is challenging to draw conclusions about the crystalline and chemical structures due to the extensive amorphization of the reactants.

2. Second stage (up to 110 min): This phase represents the "transition state" of the reaction system. At this point, it remains difficult to ascertain the crystalline and chemical structures. The mechanical energy introduced during this stage primarily contributes to the destruction of the reactants' crystal structures. The mechanochemical activation accumulates mechanical energy in the material, leading to increased potential energy and chemical reactivity.

   The peak of energy flow in the second stage represents the minimum amount of energy required to transform reactants into products in a chemical reaction. The value of the activation energy is equivalent to the difference in potential energy between particles in an intermediate configuration (known as the transition state or activated complex) and particles of reactants in their initial state. The activation energy thus can be visualized as a barrier that must be overcome by reactants before products can be formed [32].
3. Third stage (after 200 min): In this stage, formation of a distinct crystal structure of barium titanate becomes evident. Diffraction maxima at d-values characteristic for barium titanate increase in intensity. The energy introduced during the third stage, along with the energy accumulated in previous stages, is primarily used for forming stable chemical bonds and constructing the crystal structure of the product. The remaining reactants and the activated complex are sufficiently exciting, ensuring that the newly formed crystal structure of barium titanate remains intact despite the continued mechanical energy input.

Throughout the activation process, mechanical energy is introduced into the reaction system, which drives these transitions. Initially, in the first stage, energy is mainly expended on the breakdown of the crystal structures of the starting reactants, causing significant amorphization [33,34]. Mechanochemical activation also promotes transformation of the released mechanical energy into stored energy within the material, manifesting as accumulated crystal lattice distortions and an increase in the specific surface area. This enhances the potential energy and chemical reactivity of the material.

The second stage of the process represents the peak of this energy flow, where the entire reaction mass enters a transition state. After 110 min of the mechanochemical treatment, the chemical analysis of the reaction mixture sample dissolved in a 10 % acetic acid solution revealed the presence of both barium and titanium in the solution. Notably, barium titanate and titanium dioxide remained insoluble in the dilute acid, leading to two important conclusions:

- Titanium detected in the solution does not originate from free titanium dioxide or barium titanate.
- Barium detected does not come from barium titanate; part of it likely originates from unreacted barium oxide, which had not yet fully participated in the reaction described by Equation (1).

These two findings suggest the total titanium present in the acetic acid solution, along with the corresponding stoichiometric portion of barium, originates from a complex intermediate compound, $*BaO*TiO_2*$, with amorphous characteristics (hence undetectable by XRD) and partial solubility in 10 % acetic acid. Repeating XRD measurements after a three-month relaxation period did not show any changes, indicating relative stability of this intermediate phase. Based on both XRD and chemical analyses, the reaction system after 110 min of the treatment can be described as consisting of the following phases:

- amorphous titanium dioxide ($TiO_2$), insoluble in acetic acid,
- amorphous barium oxide (BaO), soluble in acetic acid,
- the amorphous activated complex ($*BaO*TiO_2*$), partially soluble in acetic acid,
- crystalline barium titanate ($BaTiO_3$), insoluble in acetic acid.

The third stage of the process is dominated by the formation of a clear and recognizable crystalline structure of barium titanate. From the amorphous structure characteristic for the second stage, the continued mechanochemical treatment results in the gradual emergence and intensification of diffraction maxima at d-values (Table 6) characteristic for barium titanate (JCPDS card No. 5-626). During this stage, the energy introduced into the reaction system via the mechanochemical reactor, along with the energy accumulated in the previous two stages, is largely consumed in forming stable chemical bonds and constructing the crystalline structure of the chemical reaction product. The remaining reactants and the assumed activated complex become so energetically excited that the formation of the product, particularly its well-defined crystalline structure, remains unaffected even by the direct influence of mechanical energy on the newly formed product crystals. The third stage represents formation of the crystalline structure during the mechanochemical synthesis, as the process of growth and development of the compound's crystal structure occurs precisely while the compound itself is being subjected to mechanical energy.

Based on the performed chemical analyses of the samples taken at different time intervals, dependence of the degree of synthesis (*S* / %) on the mechanochemical treatment duration was determined and the resulting kinetic diagram is shown in Figure 7.

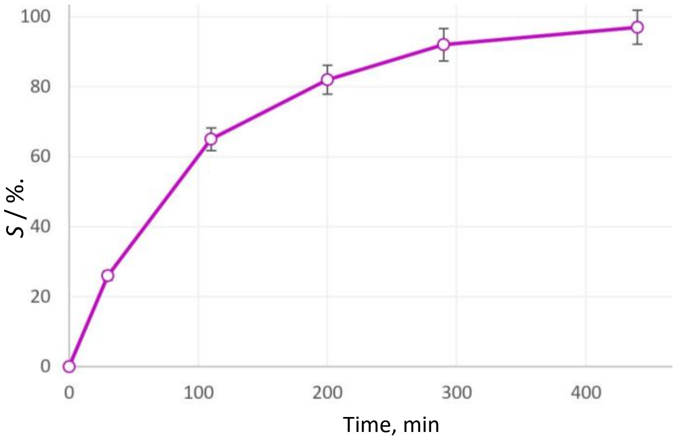

*Figure 7. Kinetics of the mechanochemical synthesis of barium titanate*

Based on the obtained kinetic diagram, the shape of the curve could be analysed. Given the nature of the chemical reaction, it can first be noted that the investigated mechanochemical process resembles a typical second-order reaction of the form: A + B → products.

However, considering the general form of the chemical reaction (Equation (1)) and the kinetic diagram, and the diffusion driven nature of the process it can be concluded that the mechanochemical process can be approximated as a pseudo-first-order reaction [21,35]. The results, which are used to generate the diagram in Figure 8, align well with the mathematical relations applicable to first-order reactions of the form: A → products, where only one reactant is involved, and the reaction rate is directly proportional to the concentration of that reactant, Equation (3) [36]:

$$-\frac{\mathrm{d}c}{\mathrm{d}t}=kc \tag{3}$$

where *c* represents the concentration of the reactant, *t* is the time, and *k* is the reaction rate constant. Introducing the variable *x*, defined as the amount of reactant consumed in the reaction over time *t*, and after performing the integration, Equation (4) is obtained:

$$\ln\frac{a}{a-x}=kt \tag{4}$$

*i.e.* Equation (5):

$$\ln\frac{1}{1-S/100}=kt \tag{5}$$

where *S* / %, represents the degree of synthesis achieved at the time *t*. When the Equation (5) is applied to the results presented in Figure 7, the resulting diagram shown in Figure 8 is obtained.

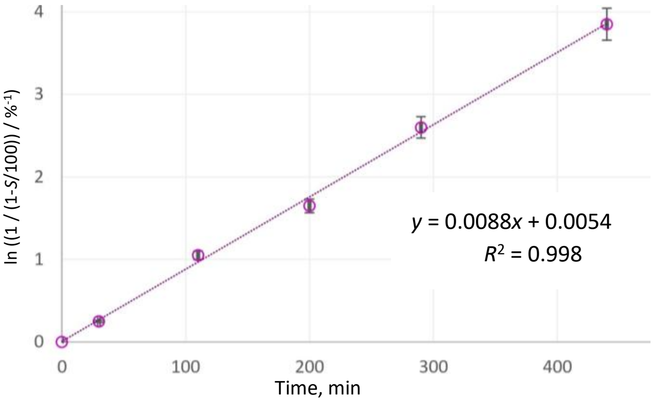

*Figure 8. Application of Equation (5) (line) on the experimental results of the mechanochemical synthesis (symbols)*

A linear dependence in Figure 8 is evident, as mathematically expressed by Equations (4) and (5), where the rate constant $k$ in this graphical representation corresponds to the slope of the line. This confirms that the mechanochemical neutralization reaction (Equation (1)), *i.e.* the mechanochemical synthesis of barium titanate follows the kinetic law of a first-order reaction. The fitted line showed a negligible intercept (0.0054), which can be attributed to experimental uncertainty, while the theoretical model predicts passage through the origin (0,0).

Given that the reaction begins with pure and inactivated reactants, which exist as elementary particles (BaO and $TiO_2$) during the mechanochemical process, it is concluded that the synthesis of barium titanate proceeds through two kinetic phases. The first phase involves collisions between the molecules of the two reactants, forming an activated complex that stoichiometrically corresponds to barium titanate but represents a unique compound in terms of its structure and chemical bonds, while the second phase involves the introduction of energy into the system, which overcomes the energy barrier along the reaction pathway, driving the chemical reaction irreversibly toward the formation of the desired product, Equation (6):

$$BaO+TiO_2 \xrightarrow{k_0} {*}BaO{*}TiO_2{*} \xrightarrow{k_1} BaTiO_3 \tag{6}$$

where $k_0$ and $k$ are the rate constants of the first and second phases of the reaction, respectively. According to the conclusion that the reaction follows first-order kinetics, the second stage of reaction (6) represents the slower phase of the overall mechanochemical synthesis of barium titanate, which means that $k_0 >> k_1$.

It can be concluded that the activation energy required to initiate the first phase of the reaction is significantly lower than the activation energy needed to convert the activated complex into the final product of barium titanate, *i.e.* to complete the second phase. The hypothesis regarding the existence of an activated complex (as an intermediate product) during mechanochemical synthesis reactions, coupled with the fact that XRD analysis of the samples after 110 min of the mechanochemical treatment did not show any changes even when repeated three months after the synthesis, supports the conclusion about the stability of the activated complex and the irreversibility of the first-phase reactions (Equation (6)), despite the transition of the reaction system from a lower to a higher energy state. The diagram showing the change in potential energy of the reactants during the mechanochemical reaction is illustrated in Figure 9.

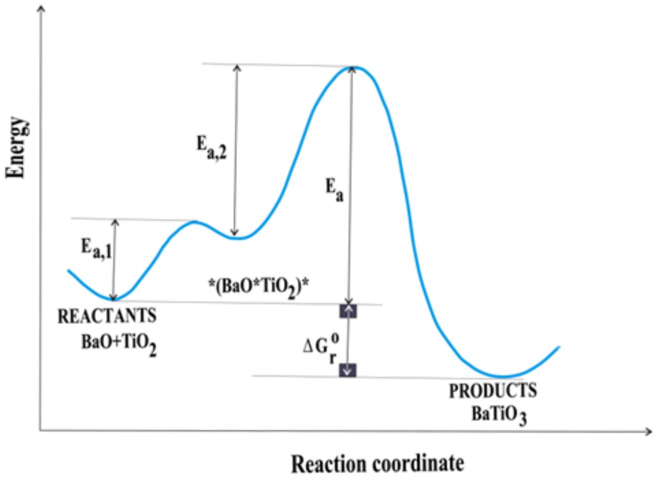

*Figure 9.Change in potential energy along the reaction coordinate*

In this study, the experiments were not conducted at varying temperatures, so it is not possible to quantitatively determine the activation energies. However, the difference in potential energy between the reactants and the products corresponds to the Gibbs free energy of reaction (Equation (1)), with a value of $\Delta G°_r$= -157.8 kJ mol$^{-1}$. The diagram representing the potential energies of the reactants and the activated complex illustrates the reaction mechanism of the mechanochemical synthesis of barium titanate, as depicted in reaction (Equation 6).

Therefore, it can be concluded that the activation energy for the first phase of reaction (Equation 6) is lower than that of the second phase. This difference in activation energies causes the rate constant for the second phase to be lower than that of the first phase, leading to the kinetic profile of a first-order reaction.

The solid-state reactions initiated by intensive milling in high-energy mills could be good choice for $BaTiO_3$ powder preparation. Intensive milling (mechanical activation) of the starting materials increases the area of contact between the reactant powder particles due to reduction in particle size and allows surfaces to come into contact [18]. In this study, high-energy mechanical activation accelerated the formation of $BaTiO_3$ without secondary phases, while previous reports also indicate that such activation can reduce the formation temperature [21].

## 4. CONCLUSION

The results of the experimental research presented in this paper have shown that $BaTiO_3$ can be obtained through a dry mechanochemical process by a neutralization reaction between BaO, as the basic reactant, and $TiO_2$, as the acidic reactant. Identification of crystalline phases formed during the reaction; monitoring of phase transformations and determination of the synthesis dynamics were successfully performed by using XRD analyses. Composition of the reaction mixture during the synthesis of $BaTiO_3$, was quantitatively analysed by AAS to determine the reaction model and reaction kinetics. To achieve a high conversion rate of 0.99, which can be considered a complete synthesis of $BaTiO_3$, it is necessary for the activation process to last 440 min. By analysing the progression of the formation of crystalline structures and by their identification, the entire process of obtaining $BaTiO_3$ can be divided into three stages: 1. the crystal structure of the BaO-$TiO_2$ reaction system is disrupted; 2. accumulation of mechanical energy increases the system's potential energy and chemical reactivity forming intermediate compounds; 3. formation of crystalline $BaTiO_3$ becomes evident. This approach highlights mechanochemical synthesis as an energy-efficient route enabling precise monitoring of reaction kinetics, while the obtained results provide a basis for optimizing similar solid-state reactions and potential industrial applications.

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# Kinetika faznih transformacija u sintezi barijum-titanata mehanohemijskom obradom

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(Naučni rad)

*Izvod*

U radu su prikazani rezultati istraživanja sinteze barijum titanata ($BaTiO_3$) na niskim temperaturama suvim mehanohemijskim postupkom. Bazni reaktant u eksperimentima je barijum oksid (BaO), dok je kao kiseli reaktant bio titanijum dioksid ($TiO_2$). Optimalna količina polaznih uzoraka za aktivaciju je bila od 50 do 150 g. U cilju praćenja reakcije između polaznih uzoraka, reakciona smeša je uzorkovana nakon 30, 110, 200, 290 i 440 min aktivacije. Za reakcije neutralizacije između BaO i $TiO_2$ korišćen je visokoenergetski vibracioni mlin sa torzionim oprugama i prstenastim radnim elementima. Produkti mehanohemijske reakcije su hemijski analizirani u cilju identifikacije neizreagovanih ostataka oksida zemnoalkalnih metala čija količina može da ukaže na stepen konverzije ili sinteze. Za identifikaciju kristalnih formi nastalih tokom reakcije i praćenje faznih transformacija korišćena je difrakciona rendgenska analiza praha (engl. X-ray powder diffraction, XRD). Dobijeni rezultati ovom analizom su omogućili definisanje dinamike sinteze. Sastav reakcione smeše, u tačno definisanim vremenskim intervalima tokom postupka sinteze, kvantitativno je analiziran atomskom apsorpcionom spektroskopijom. Cilj ovog istraživanja je bio da se tokom sinteze $BaTiO_3$ odredi reakcioni model kao i kinetika reakcije. Rezultati dobijeni u prikazanom eksperimentu su pokazali da je tokom reakcije sinteze $BaTiO_3$ u čvrstom stanju postignut izuzetno visok stepen konverzije (0,99). Uzorkovanjem reakcione smeše u pet različitih vremenskih intervala potvrđeno je prisustvo početnih prahova BaO i $TiO_2$, zatim intermedijarnih jedinjenja i na kraju konačnog proizvoda, kristalnog $BaTiO_3$. Analizom nastanka kristalnih struktura i njihove identifikacije ceo proces dobijanja $BaTiO_3$ može se podeliti u tri etape: prva etapa u kojoj se urušava kristalna struktura reakcionog sistema BaO-$TiO_2$ (do 30 min); druga etapa je nastanak prelaznog stanja gde je teško utvrditi kristalnu i hemijsku strukturu, dovedena mehanička energija sistemu se akumulira u materijalu što ima za posledicu povećanje potencijalne energije i hemijske reaktivnosti (do 110 min); treća etapa u kojoj dolazi do značajnog formiranja kristalnog $BaTiO_3$ (posle 200 min). Rezultati su pokazali da je za dati sistem potrebno 440 min mehaničke aktivacije da se izvrši potpuna reakcija neutralizacije.

*Ključne reči:* reakcija u čvrstom stanju; BaO; $TiO_2$; mehanizam reakcije; kinetika; mehanohemijska sinteza