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Original scientific paper

X-RAY STRUCTURAL ANALYSIS OF THE BaO AND TiO_2 STARTING COMPOUNDS AND INITIAL MECHANOCHEMICAL ACTIVATION

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Abstract: The aim of this research was to obtain an initial characterization of the BaO and TiO_2 components, as well as to conduct preliminary research into the possibility of activating the initial components in order to obtain barium titanate. Chemical and X-ray structural analysis of the initial components was performed. In order to determine the possibility of applying a mechanochemical activator and the activation time in which the first intermediate compounds were formed by the activation of the starting substances, the system was activated for 30 minutes. After this, an X-ray structural analysis was performed and certain changes in the crystal lattice of the starting components were made. X-ray structural analysis showed that during grinding, amorphization of the initial components occurred, which is the first stage in the process of obtaining titanate, as well as the presence of a small amount of barium titanate, which is indicating the presence of an intermediate compound in the process of finally obtaining barium titanate.

Keywords: mechanochemical activation, barium titanate

1 INTRODUCTION

Synthesis reactions that occur during mechanochemical activation are chemical reactions in the solid phase. The study of reactions in the solid state implies the existence of specific parameters characteristic of the complex state of solid matter (Korobov, 2005; Hokkaido University, 2019; Li et al., 2017; Naseer, 2005). In this type of chemical reaction, there is a direct contact of solid particles, without their dissolution and decomposition into ions. Reactions in the solid phase are only possible if they are

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thermodynamically feasible. A necessary condition is the initiation of the reaction, i.e. the supply of the required amount of energy. The initial energy must be the same or higher than the required activation energy for the desired reaction expected between the components and the conditions in which it takes place (Oleynikov et al, 1974; Gomes, 1961; DeBoer & Selwood 1954; Behrens, 2008; Criado, 1981).

Mechanochemical synthesis is solid phase reaction, without prior dissociation of reactants in the classical sense and without the mediation of solvents. As such, it cannot be based on known theories about acid-base reactions (neutralization reactions). If, as a product of a mechanochemical reaction, a chemical compound is obtained which, according to its chemical composition and other physical and chemical characteristics, is a salt of an acid and a base, and the reaction was entered with an anhydride of an acid and an oxide base of a hydroxide, such a reaction must still be considered a neutralization reaction. The mechanism of the neutralization reaction in mechanochemical processes could be set in such a way that some kind of dissociation is still ahead of the reaction, as a result of the collision of elementary particles of two reactants, where the collision must have enough energy to cause dissociation. By grinding, i.e. mechanical activation, energy is supplied to the system, interatomic bonds in the molecule are excited, bonds inside crystal lattice are broken and new states are established. At the moment of collision, the main role in the further course of the reaction is assumed by electrons from excited and broken bonds. The outcome of the reaction is conditioned by the establishment of new, stable bonds that will be built by those electrons - carriers of the reaction. In the case of mechanochemical reactions of neutralization, perhaps only Lewis' definitions of acid-base reactions (Lewis, 1916; Avvakumov, 1986), i.e. neutralization reactions, can be partially applied, in the domain of acid as an acceptor and base as an electron donor. The amount of energy required to initiate a chemical reaction has the greatest influence on the kinetics of chemical processes in the solid phase (Boldyrev, 1993).

Barium titanate is a product that can be obtained from barium oxide and titanium dioxide in a mechanochemical reactor. For the examination of the processes that occur during the reactions between substances in the solid state, and the examination of the kinetics and mechanism as well as the transition phases of intermediate compounds during the process of mechanochemical synthesis, a significant emphasis is placed on the reactions between titanium dioxide and the corresponding oxides, including barium oxide (Lazarević, 2009).

2 EXPERIMENTAL PROCEDURE

The mechanochemical activation of two oxides (BaO and TiO_2) was performed in a high-energy vibration mill with torsion springs and annular working elements, manufacturer KHD Humboldt Wedag A.G., Germany, type MH954/3. The grinding time was 30 minutes. The power of the activator motor was 0.8 kW. The mill consists of a bed and a horizontally placed shutter. The working vessel is a cylindrical vessel made of stainless steel, 40 mm deep and 170 mm inside diameter.

The working elements consist of two free concentric rings made of stainless steel with a total mass of 3 kg. The optimal amount of mechanochemically activated powders is 50-150 g. The samples were recorded and diffractometrically analysed on an automated diffractometer with a PHILIPS PW-1700 copper tube, which operates at 40 kV and 35 mA. The device is equipped with a graphite monochromator and a proportional counter, filled with xenon. The shooting angle (2θ) from 4 to 15° was used. For the experiments, barium oxide (BaO) was used as a basic reactant, and titanium dioxide (TiO_2) as an acidic reactant. No preconditions have been set for the starting components in relation to the crystal structure and granulometric composition. The optimal amount of background components that are activated in the mechanochemical reactor is from 50 to 150g. Recalculated according to reaction 1, the amount of starting substances consisted of 0.5 mol (76.7 g) BaO and 0.5 mol (39.9 g) TiO_2, so the total amount of starting material was 116.6 g.

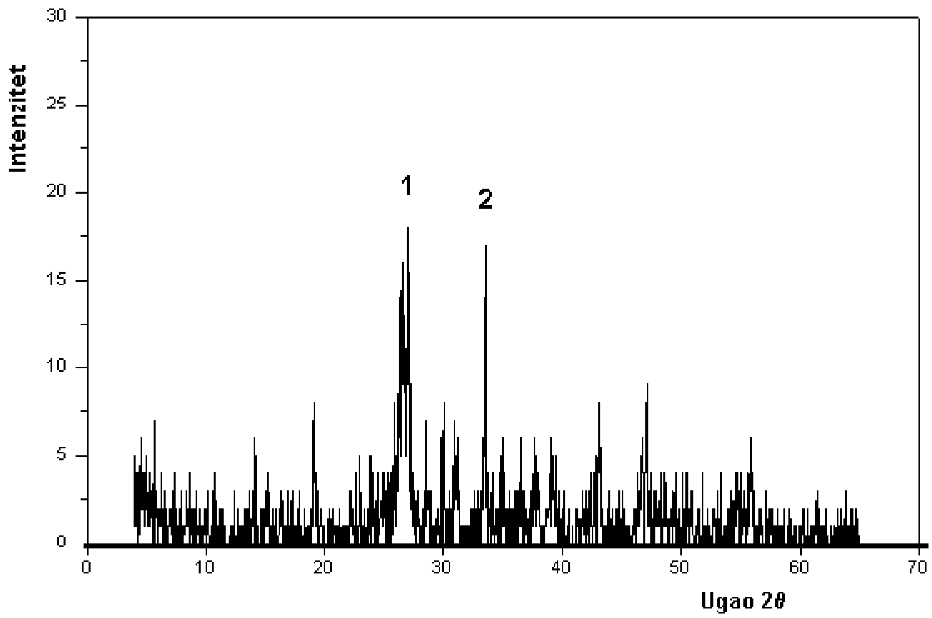
$$BaO_{(s)} + TiO_{2(s)} = BaTiO_{3(s)}\ (BaO \cdot TiO_2) \qquad \text{(Eq. 1)}$$

Barium oxide manufactured by FLUKA (Switzerland), CAS No. was used in the experiments. [1304-28-5], *pro analysi*. The chemical characteristics of BaO are given in Table 1.

Table 1 Chemical characterization of barium oxide

Content (acidimetric), min.%	98
Substances insoluble in HCl, max.%	0.005
Impurities, max.%	
Carbonates (as CO_2)	0.5000
Chlorides (Cl)	0.0050
Sulfates (SO_4)	0.0010
Total Nitrogen (N)	0.0020
Arsene (As)	0.0001
Calcium (Ca)	0.0200
Iron (Fe)	0.0050
Potassium (K)	0.0050
Sodium (Na)	0.2500
Lead (Pb)	0.0010
Loss on ignition, max.%	0.5

In order to identify barium oxide and its crystal structure, X-ray structural analysis was performed, shown in Figure 1.



Characteristic diffraction maxima of barium oxide

Pick no.	**d - value**	**Angle 2Θ**
1	3.2895	27.085
2	2.6771	33.445

Figure 1 X-ray structural analysis of barium oxide sample

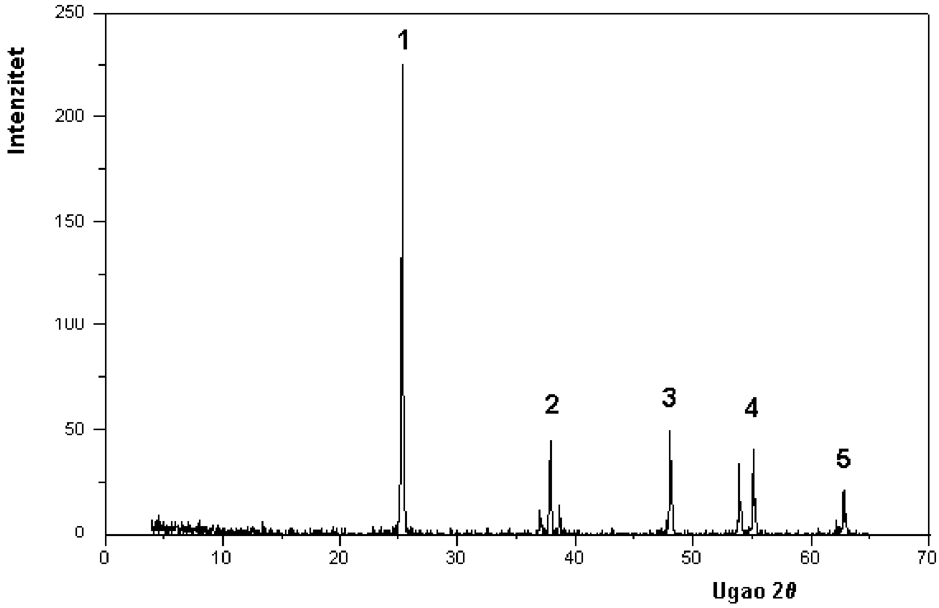
By analysing the X-ray results showed at Figure 1, it was established that it is a substance that is largely amorphized. Diffraction maxima (d-values 3.2895 and 2.6771) lead to the conclusion that the analysed sample corresponds to (poorly crystallized) barium oxide (chemical composition BaO), according to the ASTM standard (No. 22-1056).

TiO_2 manufactured by MERCK (Germany), CAS No. was used in the experiments. [13463-67-7], quality *pro analysi*. Table 2 shows the chemical composition of the titanium oxide used.

Table 2 Chemical characterization of titanium dioxide

The content, %	99.0 – 100.5
Substances soluble in water, max.%	0.5
Substances soluble in HCl, max.%	0.5
Impurities, max.%	
Heavy metals (like Pb)	0.0020
Acid-soluble antimony (Sb)	0.0002
Sulfates (SO_4)	0.0010
Total nitrogen (N)	0.0020
Acid-soluble barium (Ba)	0.0002
Arsenic (As)	0.0001
Iron (Fe)	0.0050
Acid-soluble lead (Pb)	0.0010
Zinc (Zn)	0.0005
Loss on ignition at 800 °C, max.%	0.5
Loss on drying at 105 °C, max.%	0.5

X-ray structural analysis of the starting titanium oxide and characteristic diffraction maxima are given in Figure 2.



Characteristic diffraction maxima of titanium dioxide

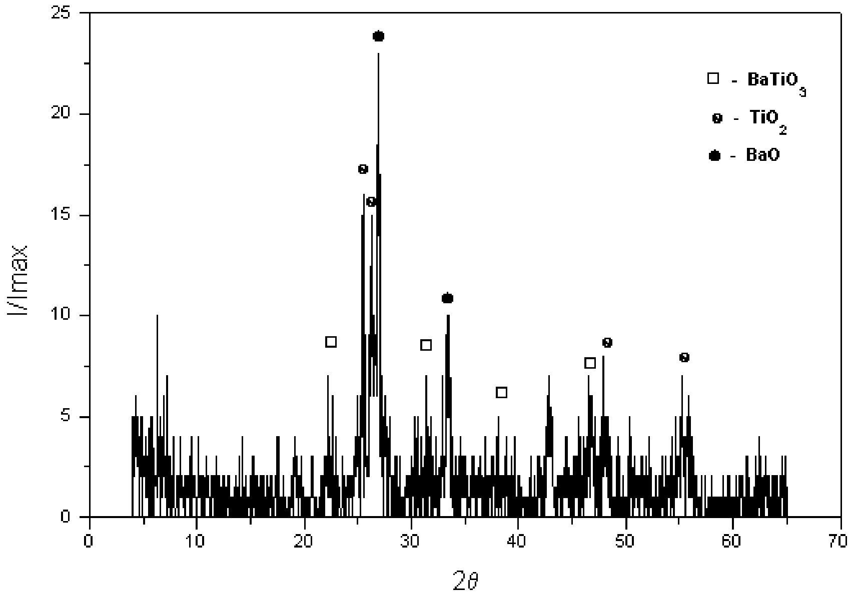
Pick br.	d - value	Angle 2 Θ
1	3.5133	25.330
2	2.3778	37.805
3	1.8926	48.035
4	1.6667	55.055
5	1.4806	62.700

Figure 2 X-ray structural analysis of titanium dioxide sample

During the experiments, a sample was taken from the reaction system and its X-ray structural analysis was performed. The activation of the starting components initially lasted 30 minutes, in order to determine whether this time is sufficient to start the chemical reaction process in the solid phase. For the analysis of the chemical composition of the system, depending on the activation time of the starting substances, the atomic absorption spectrophotometric method was used.

3 RESULTS AND DISCUSSION

X-ray structural analysis of the mixture of starting components was performed after 30 minutes of activation. In this way, both starting components and products of mechanochemical processes are identified and monitored. Figure 3 shows the X-ray structural analysis of the sample after 30 minutes of mechanochemical treatment.



Characteristic diffraction peaks (20 peaks registered)

Pick br.	Characteristic for substance	d – value	Angle 2Θ
1	**$BaTiO_3$**	3,9940	22,24
2	TiO_2	3,4937	25,47
3	TiO_2	3,3878	26,28
4	BaO	3,3099	26,91
5	**$BaTiO_3$**	2,8273	31,62
6	BaO	2,6794	33,41
7	**$BaTiO_3$**	2,3231	38,73
8	**$BaTiO_3$**	1,9461	46,63
9	TiO_2	1,8848	48,24
10	TiO_2	1,6545	55,49

(The remaining 10 registered peaks belong to the noise domain)

Figure 3 X-ray structural analysis of the reaction system sample (BaO+TiO_2) after 30 minutes of mechanochemical treatment

The broadening of the diffraction lines and their insignificant intensity indicate that after 30 minutes there was a significant disruption of the crystal structure of the initial reactants, especially titanium dioxide, whose crystal structure was very clearly expressed before the start of the reaction (Figure 2). The analysis of the registered peaks and the corresponding diffraction angles confirmed the presence of initial reactants, but also the beginnings of the formation of the product - barium titanate at some of the characteristic diffraction angles for this substance.

Based on the diffractogram, it can be concluded that in these 30 minutes of activation (grinding) the first phase of activation took place and it is the phase of progressive destruction of the crystal structure of the reactants. It was also determined the existence of a compound that, according to its chemical composition, contains all the components of barium titanate, but it is still an intermediate compound, which indicates the fact that during this grinding time, the beginning of a chemical reaction between the initial components took place. The presence of pure oxides as well as traces of barium titanate indicates that activation in the sense of a solid-state chemical reaction has begun during this initial activation time.

Observing the reaction, the mechanical energy that is imputed into the reaction system, in this phase is mainly spent on the destruction of the crystalline structure of the initial reactants and their significant amorphization. The mechanochemical activation of individual substances (as well as the combination of two or more substances) leads to the transformation of the released mechanical energy and its accumulation in the treated material in the form of accumulated deformations of the crystal lattice, an extremely developed and active specific surface of the material, whereby the material is brought to an elevated level of energy content. This results in an increased degree of potential energy, i.e. chemical reactivity of the material.

Considering that the reaction was started with pure and inactivated reactants, which as elementary particles (BaO and TiO_2 molecules) exist as reactants during the mechanochemical reaction, it can be concluded that the first phase of the reaction takes place in the first 30 minutes. It involves mutual collisions between the molecules of two reactants, resulting in the formation of an activated complex, which stoichiometrically corresponds to the chemical composition of barium titanate, but in terms of structure and characteristics of chemical bonds, it represents a special compound. The second stage should be the further introduction of energy into the reaction system, which assumes that the energy barrier on the reaction path to the product of the reaction should be overcome, so the chemical reaction irreversibly flows towards the expected product.

In further experiments, it is planned to extend the grinding time, and to monitor the activation products, which would determine the exact time required in the given device for the starting components to completely chemically react and give the desired product, barium titanate.

Acknowledgments

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REFERENCES

A. KOROBOV, Simple Chemical Reactions in the Solid State: Towards Elaborating a Conception, *Foundations of Chemistry* volume 7, pages 307–314 (2005)

HOKKAIDO UNIVERSITY, Boosting solid state chemical reactions, Public Release: 10-Feb-2019 Accessed on [20.03.2023.] Available online [https://www.global.hokudai.ac.jp]

LI, Det al. (2017, September). Solid-state chemical reaction synthesis and characterization of lanthanum tartrate nanocrystallites under ultrasonication spectra. In *IOP Conference Series: Materials Science and Engineering* (Vol. 242, No. 1, p. 012023). IOP Publishing.

NASEER, H. Study of solid state reactions, PhD Thesis, 2005.

OLEYNIKOV, N. N., TRETYAKOV, Y. D., & SHUMYANTZEV, A. V. (1974). Concerning the activation energy of solid state reactions. *Journal of Solid State Chemistry*, *11*(4), 340-343.

GOMES, W. (1961). Definition of rate constant and activation energy in solid state reactions. *Nature*, *192*, 865-866.

DEBOER, F. E., & SELWOOD, P. W. (1954). The activation energy for the solid state reaction γ-Fe2O3→ α-Fe2O3. *Journal of the American Chemical Society*, *76*(13), 3365-3367.

BEHRENS, F. H. M., Institute of the Max Planck, Solid State Kinetics Society Department of Inorganic Chemistry, 2008.

CRIADO, J. M. (1981). On the determination of the activation energy of solid-state reactions from the maximum reaction rate of isothermal runs. *Journal of thermal analysis*, *21*, 155-157.

LEWIS G.N. The Atom and the Molecule in *Journal of American Chemical Society*, vol.38, no.4 (1916)

AVVAKUMOV, E.G., Mekhanicheskie metody aktivacii khimicheskih procesov, Izd. Akad. Nauk SSSR (1986)

BOLDYREV, V.V., *J. Solid State Ionics,* V63, N5, 537 (1993)

LAZAREVIĆ, Z. Ž., BOBIĆ, J., ROMČEVIĆ, N. Ž., PAUNOVIĆ, N., & STOJANOVIĆ, B. D. (2009). Study of barium bismuth titanate prepared by mechanochemical synthesis. *Science of Sintering*, *41*(3), 329-335.