

Properties of mechanochemically pretreated precursors of doped BaTiO₃ ceramics

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The properties of doped BaTiO₃ ceramics prepared from mechanically activated precursors (BaCO₃, TiO₂, PbO), dopant (Sb) and admixtures (SiO₂, Al₂O₃) were investigated. Mechanical activation of the mixture 1.00 BaCO₃ + 1.15 TiO₂ + 0.10 PbO brings about an increase in its specific surface and partial amorphization of BaCO₃; Ba, O and C occur in the surface of this mixture in at least two chemically different states. BaTiO₃ obtained from the above mentioned mechanically activated precursors by high-temperature solid-state synthesis at 1100°C consists of homogeneous particles with a narrow particle size distribution.

1. Introduction

BaTiO₃ exhibiting the tetragonal perovskite structure [1] belongs among piezoelectric minerals with interesting electrophysical properties. Barium titanate in pure form is a dielectric. However, it becomes a semiconductor after addition of dopants and shows a positive temperature coefficient of resistance (PTCR) [2]. The PTCR effect is dependent on the position of the Curie point at which the symmetry of the crystal decreases owing to transformation of a cubic lattice into a tetragonal lattice, or the paraelectric (high-temperature) phase turns into the ferroelectric (low-temperature) phase. Barium titanate also appears to be attractive as a ceramic-type agent for immobilizing high-level radioactive waste in the so-called SYNROC process [3].

BaTiO₃ powders are traditionally prepared by solid-state reaction between barium carbonates or oxides and TiO₂ at temperatures over 1000°C [4, 5]. The microstructure of BaTiO₃ originated in the process of high-temperature recrystallization is significantly dependent on the character of the input powdered mixture (size homogeneity, surface activity, particle size) and on the presence of liquid-forming admixtures or growth inhibitors which simultaneously represent the dopants (Sb, Nb) used in this case. That is why new methods of preparation are sought for obtaining fine powders with new processing properties (e.g. the sol-gel process, peroxide route, titanyl-oxalate process, cryochemical route, plasmochemical route).

One of the possibilities for influencing the properties and reactivity of solid substances is their mechanochemical pretreatment in high-intensity mills [6–8]. The increase in reactivity obtained by produ-

cing ceramic precursors with a high specific surface area and a narrow size distribution provides the energy storage necessary for sintering to high density [9, 10]. In recent mechanochemical ceramic technology has become a subject of discussion [11, 12].

The aim of this study has been to obtain information about the surface-structural properties of mechanochemically pretreated BaCO₃-TiO₂-PbO powders which are the precursors of doped BaTiO₃ ceramics.

2. Experimental procedure

2.1. Materials

The investigations were carried out with chemically pure substances, i.e. BaCO₃ (for ferroelectrics), TiO₂ (anatase for ferroelectrics) and PbO (yellow). All chemicals were products of Lachema (Czech Republic). Before the experiments a mixture with molar ratio BaCO₃:TiO₂:PbO = 1.00:1.15:0.10 (denoted BTP) was homogenized by stirring in methanol for 60 min.

2.2. Mechanical activation

The samples of BTP (20 g) were mechanically activated in a planetary mill (Pulverisette 4, Fritsch, Germany) under the following conditions. Ball charge: 11 balls, 20 mm in diameter plus 15 balls, 10 mm in diameter; ball material: agate; time of grinding: 30–240 min in methanol (35 ml); relative acceleration of the mill: $b/g = 12.4$.

2.3. Surface area

The specific surface area S_A was determined by the low-temperature nitrogen adsorption method in a

Gemini 2360 Sorption apparatus (Micromeritics, USA).

2.4. Infrared spectroscopy

Infrared spectra were obtained with a Specord 75 spectrometer (Zeiss, Germany) using the KBr disc technique.

2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopic measurements were carried out on an ESCA 3 Mk II apparatus (VG Scientific, Great Britain) in 10^{-6} Pa vacuum. The electrons were excited by AlK_{α} radiation ($h\nu = 1486.6$ eV). The transmission energy of the electron analyser was 20 eV and the width of the entrance slit of the analyser was equal to 4 mm. The binding energies corresponding to barium, titanium and lead were determined by fitting the XPS spectra. The values of binding energies were measured with an accuracy of ± 0.2 eV and the estimated error in stoichiometric factors was $\pm 15\%$.

2.6. X-ray diffractometry (XRD)

The X-ray diffraction phase analysis was performed on a diffractometer Dron 2.0 (Techsnabexport, Russia) in the following regime. Radiation: CuK_{α} , 3 kV, 20 mA; time constant: 1 s; limit of impulse measurements: 10 s^{-1} ; rate of movement of detector: $2^{\circ}\text{ min}^{-1}$; paper drive: 2.4 m^{-1} .

2.7. Scanning electron microscopy (SEM)

The particle morphology was monitored on a BS 340 scanning electron microscope (Tesla Brno, ČSFR).

2.8. Synthesis of $BaTiO_3$ and high-temperature sintering

The mechanically activated BTP mixture was heated for 1 h at 1100°C . Dopant in the amount of 0.3 mol % Sb and the admixture ($SiO_2 + Al_2O_3$) in the amount of 0.2 wt % were added to the developing $BaTiO_3$ phase. After homogenization lasting 60 h and taking place in a ball mill in the medium of methanol and after drying, the powdered mixture was compacted to discs (7 mm diameter, width 3 mm) and sintered at 1350°C .

3. Results and discussion

3.1. Surface area

The specific surface area of mechanically activated BTP samples increases from the value of $4.2\text{ m}^2\text{ g}^{-1}$ found for a non-activated sample to $5.1\text{ m}^2\text{ g}^{-1}$ for a sample activated for 240 min (Fig. 1). The continuous increase in surface indicates a gradual decrease in size of the BTP particles. The application of a liquid medium (CH_3OH) in the process of activation prevents aggregation of the particles.

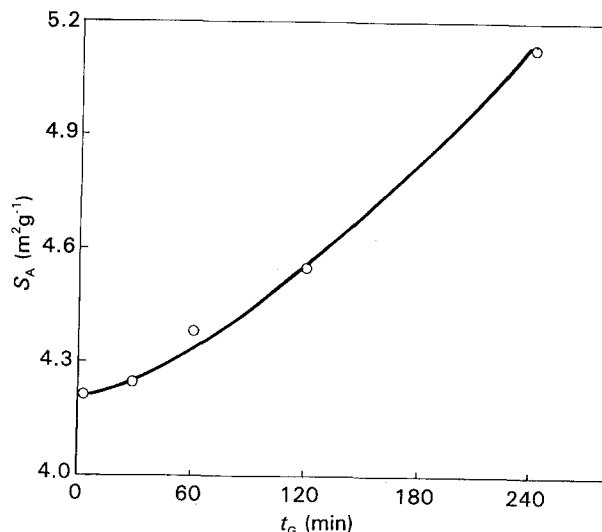


Figure 1 Variation of specific adsorption surface S_A of the mechanically activated mixture $BaCO_3 + TiO_2 + PbO$ with activation time t_G .

3.2. X-ray diffractometry

According to the results obtained by XRD the starting (non-activated) mixture contains $BaCO_3$ as witherite (ASTM 5-378), TiO_2 as anatase (ASTM 21-1 272) and orthorhombic PbO (ASTM 5-570) [13]. The relative disordering (amorphization) of the structure of $BaCO_3$ and TiO_2 defined by the ratio $I_r = I_o/I$ (I_o = height of the peak of non-activated sample, I = height of the peak of activated sample) is represented in Fig. 2 as a function of the time of mechanical activation. The dependence obtained for both components of the BTP mixture shows that $BaCO_3$ gradually becomes amorphous with the time of activation, while the structure of anatase remains unchanged.

3.3. Infrared spectroscopy

The infrared spectra of the BTP mixture are represented in Fig. 3 for a non-activated sample (curve 1) as well as for samples mechanically activated for 60 and 240 min (curves 2 and 3). The bands were assigned to individual components of the mixture on the basis of comparison with the spectra of pure substances ($BaCO_3$, TiO_2) and according to the literature [14]. The broad band W at $\bar{\nu} = 3400\text{--}3500\text{ cm}^{-1}$ corresponds to water in the KBr tablet. In the spectra of activated samples we can observe a new broad band Q in the region $\bar{\nu} = 1100\text{--}1300\text{ cm}^{-1}$. This band already starts to appear in the case of the sample activated for 30 min and gradually becomes more distinct with the time of activation. This band can be attributed to SiO_2 which was incorporated into samples during mechanical activation and had its origin in the material of the grinding chamber and grinding balls.

3.4. X-ray photoelectron spectroscopy

The lines of $Ba3d$, $Ti2p$, $C1s$ and $Pb4f$ in the XPS spectra were measured for a non-activated BTP sample and samples activated for 30 and 240 min. The

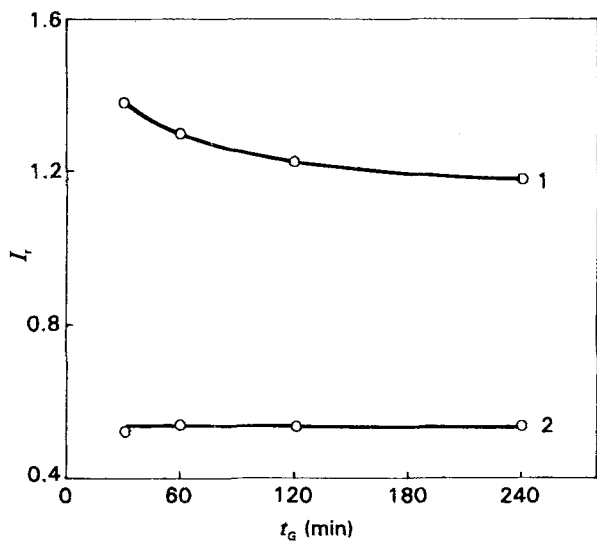


Figure 2 Dependence of relative disordering of the structure of (1) witherite and (2) anatase in the mechanically activated mixture $\text{BaCO}_3 + \text{TiO}_2 + \text{PbO}$ on activation time t_G .

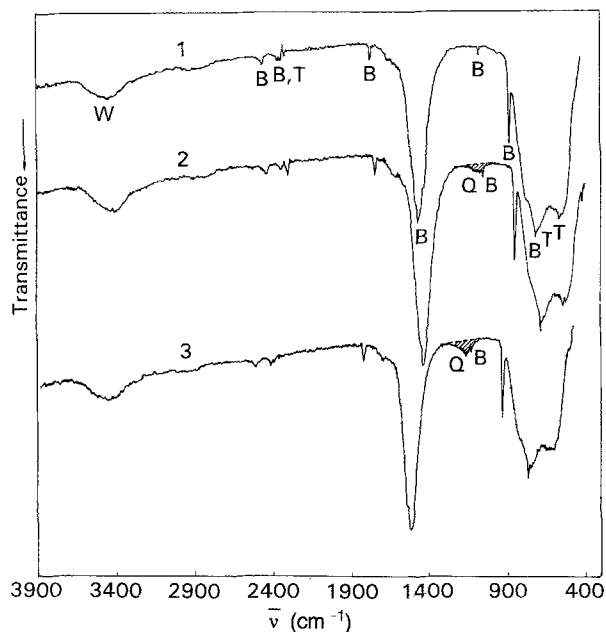


Figure 3 Infrared spectra of the mixture $\text{BaCO}_3 + \text{TiO}_2 + \text{PbO}$. Time of mechanical activation: (1) 0 min, (2) 60 min, (3) 240 min; (B) BaCO_3 , (T) TiO_2 , (W) H_2O , (Q) SiO_2 .

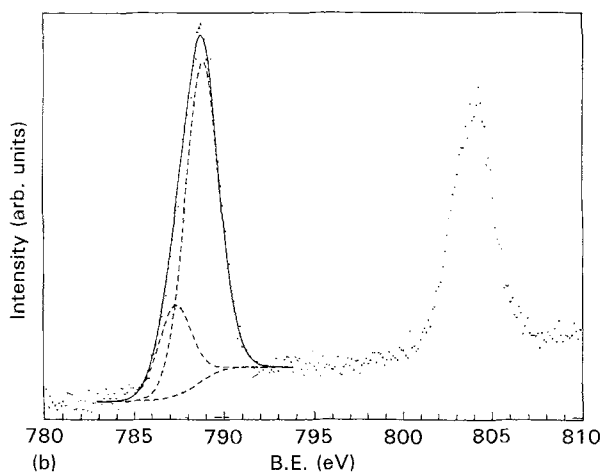
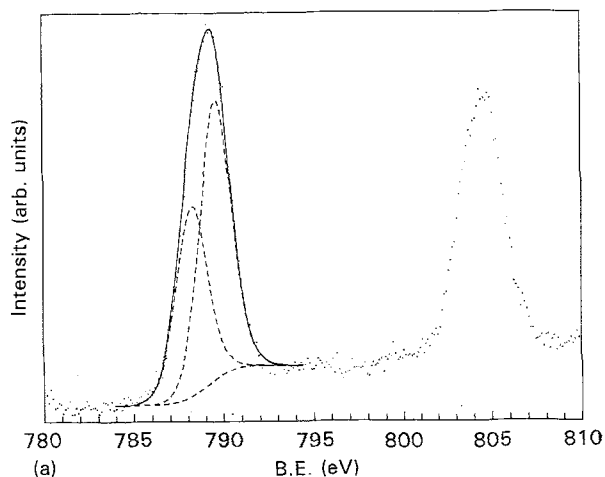


Figure 4 XPS spectrum of $\text{Ba}3d$. Time of mechanical activation: (a) 0 min, (b) 240 min.

shape of spectral lines of $\text{Ba}3d_{5/2}$, $\text{O}1s$ and $\text{C}1s$ represented in Figs 4–6 shows that these elements are present in at least two chemically different states (further denoted α and β). For finding the differences between surface composition and bulk composition the samples were treated by the argon ion sputtering technique under conditions leading to removal of a surface layer of about 120 nm depth. The results of the measurements of binding energies and line widths of individual elements are given in Table I. A comparison of the results with those obtained by measuring standards (BaCO_3 , BaO , TiO_2 and

TABLE I Binding energies (eV) and widths of the measured lines at half-height (in parenthesis) of the mixture $\text{BaCO}_3 + \text{TiO}_2 + \text{PbO}$, with and without argon ion sputtering

Element	No mechanical activation		240 min mechanical activation	
	Not sputtered	Sputtered	Not sputtered	Sputtered
$\text{Ba}3d_{5/2}$	778.2(2.1)	–	778.4(2.2)	–
	779.5(2.1)	779.6(2.2)	779.9(2.2)	779.4(2.3)
$\text{Ti}2p_{3/2}$	457.7(1.7)	457.7(2.0)	458.0(3.2)	457.4(2.2)
$\text{O}1s$	529.2(2.1)	529.3(2.1)	529.5(2.1)	529.3(2.1)
	531.3(2.1)	531.3(2.1)	531.5(2.1)	531.2(2.1)
$\text{C}1s$	284.8(2.5)	284.8(2.2)	284.8(2.4)	284.8(2.0)
	288.5(2.5)	288.8(2.8)	288.1(2.4)	–
$\text{Pb}4f_{7/2}$	137.8(1.9)	136.5(3.5)	137.9(2.0)	–

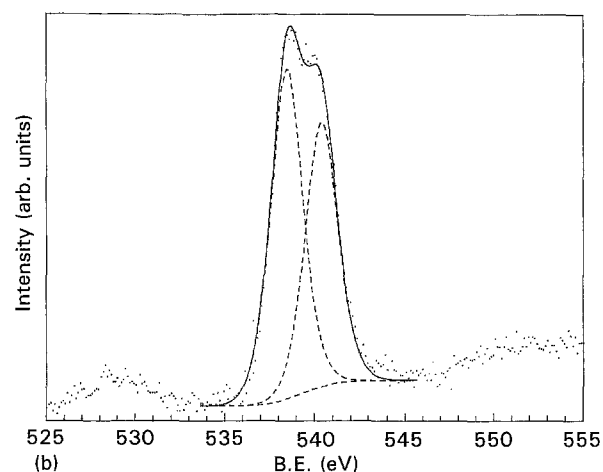
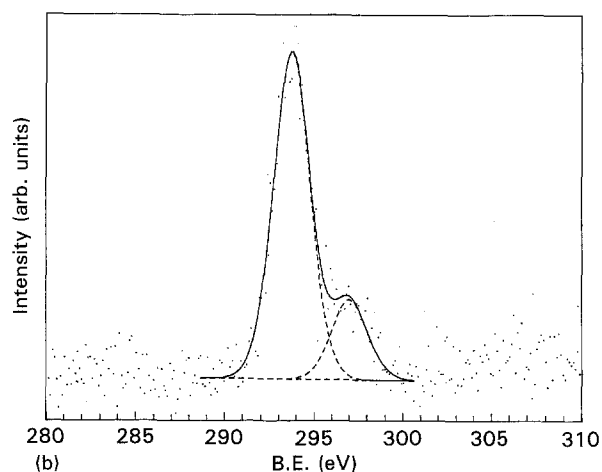
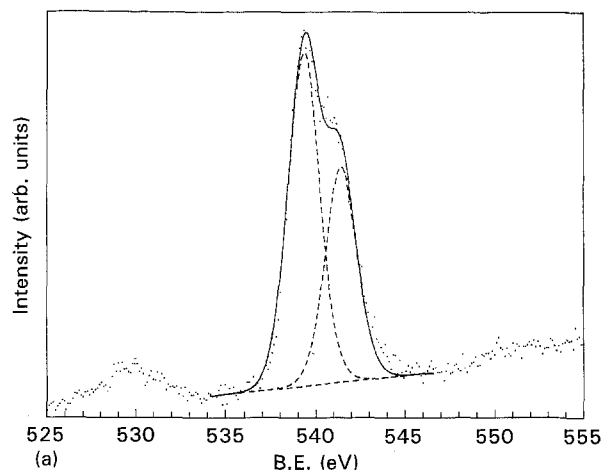
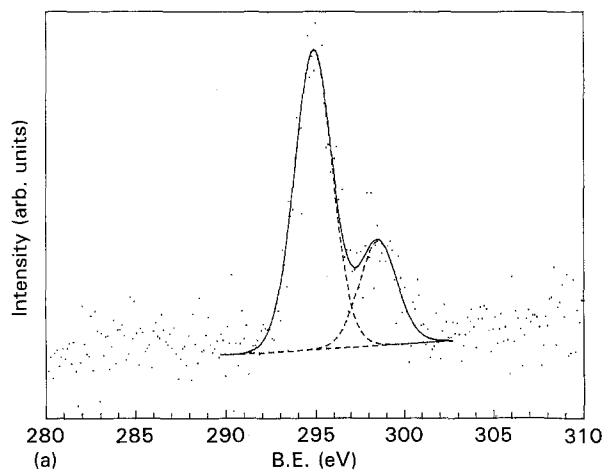


Figure 5 XPS spectrum of C1s. Time of mechanical activation: (a) 0 min, (b) 240 min.

Figure 6 XPS spectrum of O1s. Time of mechanical activation: (a) 0 min, (b) 240 min.

BaTiO₃) and with literature data [15–18] enabled us to identify the chemical states of the elements and to calculate their relative atomic concentrations in the samples studied (Table II). Theoretical photoionization cross-sections [19] were used to convert peak areas into the elemental concentrations.

It results from the data presented in Table II that the content of barium ^αBa with a lower value of binding energy decreases with increasing time of mechanical activation. If the surface layer is removed by argon ion sputtering this form of barium cannot be observed at all. Simultaneously, the proportion of oxygen ^αO decreases. The form ^αBa and to a certain extent the form ^αO is to be attributed to the surface Ba(OH)₂ which is washed out of the surface of BTP samples with increasing time of mechanical activation. Barium ^βBa corresponds to BaCO₃, as do parts of ^βO

and ^βC. A part of ^αO oxygen is bonded in TiO₂ and PbO. We should mention that ion sputtering brings about decomposition of the CO₃²⁻ group and reduction of Ti and Pb oxides. ^αC comes from hydrocarbons present on the sample surface. Titanium and lead correspond to oxides of the BTP mixture present in the surface as well as in the bulk of the samples. The proportion of lead in the surface is raised and mechanical activation promotes its homogeneous distribution in the whole volume of BTP samples.

3.5. Scanning electron micrographs

The size distribution and homogeneity of recrystallized grains of the doped BaTiO₃ ceramics was determined by means of SEM in BTP samples mechanically activated for 30 and 240 min and subjected to

TABLE II Relative proportion of individual forms of elements in the mechanically activated mixture BaCO₃ + TiO₂ + PbO

Mechanical activation (min)	Argon ion sputtering	Relative proportion of elements
0	No	^α Ba _{0.7} ^β Ba _{1.0} Ti _{1.4} ^α O _{4.9} ^β O _{3.1} ^α C _{2.9} ^β C _{1.0} Pb _{0.15}
	Yes	^β Ba _{1.0} Ti _{0.9} ^α O _{2.9} ^β O _{0.8} ^α C _{1.3} ^β C _{0.2} Pb _{0.04}
30	No	^α Ba _{0.4} ^β Ba _{1.0} Ti _{1.1} ^α O _{3.8} ^β O _{2.8} ^α C _{5.2} ^β C _{0.8} Pb _{0.09}
240	No	^α Ba _{0.3} ^β Ba _{1.0} Ti _{1.1} ^α O _{3.3} ^β O _{2.7} ^α C _{3.9} ^β C _{0.9} Pb _{0.09}
	Yes	^β Ba _{1.0} Ti _{1.0} ^α O _{2.9} ^β O _{0.7} ^α C _{1.6} Pb _{0.04}

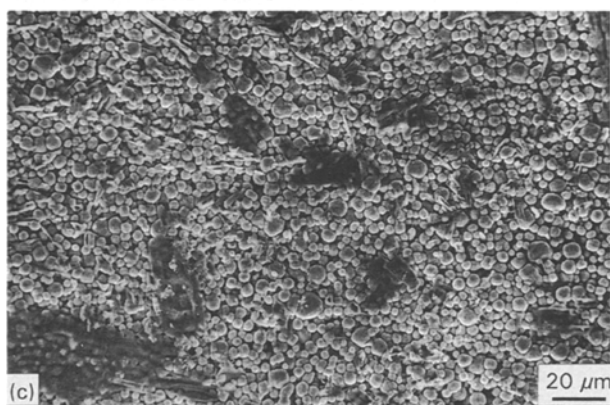
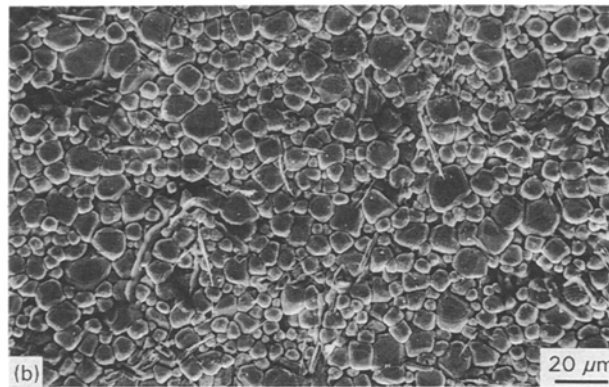
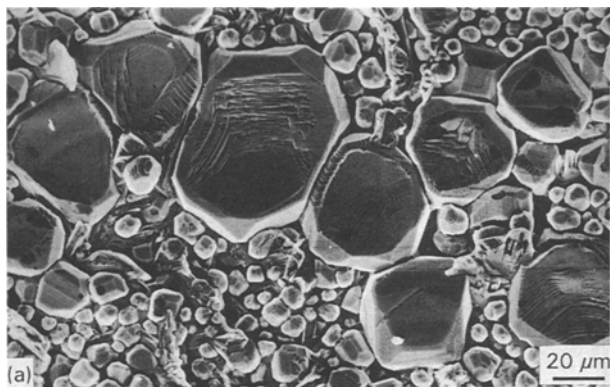


Figure 7 Scanning electron micrographs of BaTiO₃. Time of mechanical activation: (a) 0 min, (b) 30 min, (c) 240 min.

subsequent thermal treatment. It can be seen in Fig. 7 that the structure of these samples is characterized by homogeneous grains without observable growth, the grain size being below 4 μm . The differences in structure between mechanically activated samples are minimal, but we can observe that the sample activated for 240 min contains a higher content of "liquid phase" consisting of quartz which was incorporated into samples due to abrasion of the agate vessel and balls. Addition of SiO₂ has an influence on the electrical properties of BaTiO₃ ceramics [20] and mechanical activation in the presence of this substance can favour its intentional and homogeneous distribution in the bulk of samples.

4. Conclusions

1. Mechanical activation of the mixture BaCO₃ + TiO₂ + PbO produces an increase in its specific surface and a partial amorphization of BaCO₃. SiO₂ was identified in the products of activation by the method of infrared spectroscopy. It was incorporated into the mixture by abrasion of the grinding apparatus (agate).

2. Analysis of the Ba3d, O1s and C1s XPS spectra has shown that these elements occur in the surface of the mechanically activated mixture in at least two chemically different states.

3. BaTiO₃ obtained by high-temperature solid-state synthesis from the mechanically activated precursors consists of homogeneous particles with a narrow particle size distribution.

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