

Nanosized BaTiO₃ powder prepared via mechanochemical activation

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Abstract: The technological possibilities for the synthesis of barium-titanate phases were investigated by applying mechanochemical activation (from 30 min. to 2 h) of the starting charges and thermal treatment of the compositions up to 900°C (with an isothermal delay of 1 h). The applied laboratory regime for the preparation of the experimental samples is in accordance with the preliminary thermodynamic calculations. The identification of the obtained phases was carried out by X-ray phase analysis (XRD). Based on the experimental results, the necessary technological conditions for the synthesis of titanate monophasic product by heat treatment at lower temperature values than those typical for standard classical synthesis have been established. The potential possibilities of application of the synthesized phases for the deposition of thin layers on metal surfaces and the preparation of various coatings with different functional purposes are considered.

Keywords: MECHANOCHEMICAL ACTIVATION, BARIUM TITANATE PHASES, LOW TEMPERATURE SYNTHESIS

1. Introduction

The development and application of various synthesis methods allows obtaining materials with diverse properties, structure and functional characteristics [1-5]. A number of authors investigate the processes of phase formation in experimental polycrystalline compositions subjected to mechanochemical treatment [6-17] under different technological conditions. In systems subjected to mechanochemical activation, a significant decrease in temperature [10-15] and isothermal holding time necessary for the synthesis of the investigated compounds (compared to classical methods) was found. It has been established that the amorphization [14] of the reagents under the influence of mechanochemical processing favors the formation of nanosized crystalline products. By applying direct mechanochemical synthesis in laboratory conditions, crystalline phases with different structure and properties were obtained [6-16].

In mechanochemical activation of the reagents, the main technological method is the application of intense friction and impact [18-20]. To achieve this effect, the batches prepared are subjected to processing in high-energy mill facilities (planetary mills equipped with suitable grinding bodies, vibrating mills and other). The nature of the ongoing processes and the structure of the obtained products are determined by a number of factors [11-19]: specificity of the individual components, presence of additional technological additives, initial composition of the batches, initial humidity of the batches, mass of the batches, ratio between the mass of the grinding bodies and the mass of the charges, duration of applied mechanochemical treatment (from minutes to days), speed of the mechanochemical processing of the reagents, specificity of the gas environment during processing, technical characteristics of the used mill, type of grinding bodies (agate, corundum, porcelain and others), mass, volume and number of grinding bodies and others.

In the specialized literature experimentally established reaction stages characteristic of the systems subjected to mechanochemical treatment are presented and some theoretical ideas and hypotheses about the mechanism of the processes are presented. For reagents subjected to mechanical processing particle sizes decrease, specific surface area increases, structural defects are generated, active centers are formed, structural and thermodynamic instability is initiated, and elevated reactivity. It is assumed that in the process of intense tribomechanical impact separate localized zones with elevated temperature values are distinguished [13-20], which provokes the thermal decomposition of thermally unstable components, accompanied by the release of other reaction products that actively participate in the processes. In accordance with the specificity of the reagents and the mode of mechanochemical treatment, conditions arise for various phase and structural transformations in the reaction system: amorphization, change in the temperature intervals of conversion and polymorphic transitions, lowering the temperature of chemical reactions, complex of chemical reactions, identification of new reaction stages uncharacteristic of identical compositions not subjected to mechanochemical processing. With some

reaction compositions, even with relatively short periods (10 min) of mechanochemical treatment, conditions are created for the formation of new phases [14].

Due to the technological advantages of low-temperature syntheses, carried out after mechanochemical activation, and especially of direct mechanochemical syntheses (without heat treatment), the perspective of applying these methods in obtaining materials of significant applied importance acquires significant importance [16-18]. In this aspect, barium titanate BaTiO₃ is of interest, which finds wide and permanent application in electronics and other technical fields. As an alternative technological approach, some authors investigate the possibilities of obtaining BaTiO₃ by applying mechanochemical methods [10-20].

2. Experimental

The aim of the present work is to study the phase composition of experimental compositions obtained from batches prepared from BaCO₃ (Alfa Aesar, pa 99.9 %) TiO₂ (anatase) (Alfa Aesar, pa 99.9 %), Bi₂O₃ (Alfa Aesar, pa 99.8 %) and doping components introduced into the general composition in the form of oxides, subjected to mechanochemical activation (up to 2 h) and heat treatment up to 900°C (with an isothermal hold of 1 h).

In a Fritsche Pulverisette 7 planetary mill with steel pots and grinding bodies, the powdery starting components, calculated in advance with the required stoichiometric composition, are placed at a rotation speed of 500 rpm (revolutions per minute). The powders are mixed for up to 2 hours in the presence of isopropanol in order to good homogenization of the mixture and destruction of agglomerates.

After analyzing the obtained data, the guidelines for optimizing the technological regime for obtaining a single-phase final product from BaTiO₃ (tetragonal phase) doped with Bi by applying mechanochemical activation and heat treatment at temperatures significantly lower than those required for classical synthesis at standard conditions.

For the purpose of mechanochemical synthesis, preliminary thermodynamic calculations were carried out in order to determine temperatures at which phases with desired properties can be obtained. The possibilities of obtaining a single phase of BaTiO₃ from different starting substances are presented in table 1.

Table 1: Thermodynamic parameters for barium titanate synthesis

Compounds	ΔH_{298}° cal/mol	ΔS_{298}° cal/mol grad	C_{p25}
BaCO ₃	-295000	26,8	20,40
BaO	-135000	16,08	10,82
Ba(OH) ₂	-258	24,8	
BaTiO ₃	-397,600	25,82	
TiO ₂ (анатаз)	-218,100	11,93	13,23
CO ₂	-94052	51,06	
H ₂ O	-57798	45,106	

3. Results and Discussion

DTA (Differential Thermal Analysis) and Thermogravimetry (TG) are presented in figures (Fig. 1).

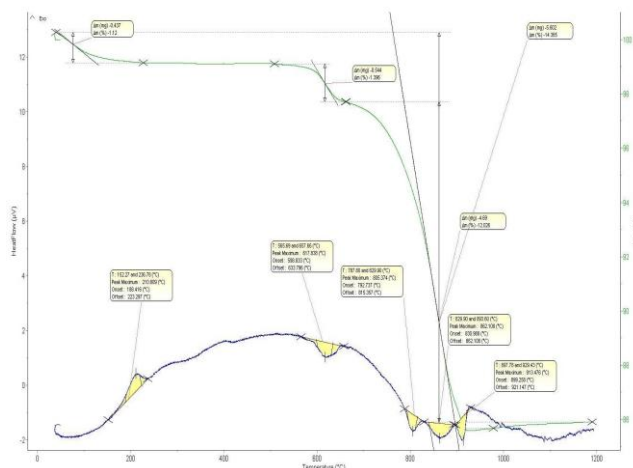


Fig.1 DTA and TG of BaTiO₃ raw materials.

Fig. 1 shows the DTA and TG curves of the barium titanate parent component BaTiO₃. The DTA curve shows one exothermic peak in the range 188°C to 223°C and four endothermic peaks in the range 598÷693°C; 830÷862°C, 899÷921°C. Endothermic behavior is accompanied by a weight loss of approximately 14%. From the figure, endothermic and exothermic peaks are found during heat treatment up to a temperature of 1000°C, while the thermo-gravimetric (TG) curve shows a weight loss of 14% upon annealing to the same temperature. In the temperature range from 430 to 1000°C, the TG curve shows a 15.8% weight loss, which takes place in three consecutive stages; characterized by three DTA peaks at 633, 862, and 921°C. Maximum weight loss is observed at 915°C.

X-ray analysis was performed using a Bruker D8 Advance automatic powder X-ray diffractometer with CuK α radiation (Ni filter) and registration by a LynxEye solid-state detector. The X-ray spectrum was recorded in the angular range from 10 to 80° 2 θ with a step of 0.02° 2 θ and a counting time of 17.5 s/step. Qualitative phase analysis was performed using the International Center for Diffraction Data (ICDD) PDF-2(2009) database.

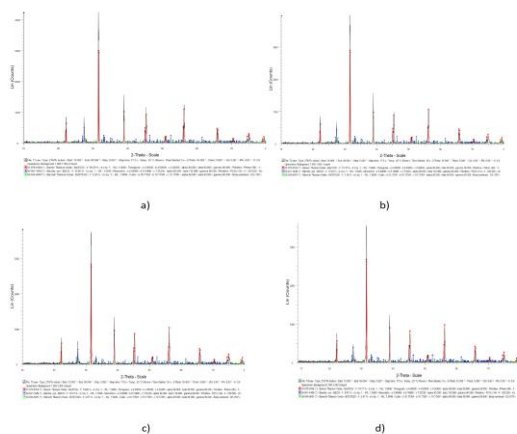


Fig.2 XRD analysis of the synthesized crystalline phases BaTiO₃, Bi₁₂TiO₂₀, Bi₂O₃

The presence of the crystalline phases was established: BaTiO₃ (dominant phase, red marking), Bi₂O₃ (blue marking) and Bi₁₂TiO₂₀ (green marking). The recorded predominant barium titanate (tetragonal shape) represents the synthesized target phase. From the presented radiographs (fig. 2 a, b, c, d), it is possible to trace the dependence and change of some of the characteristics of the compositions with increasing homogenization time and the applied mechanochemical treatment in the interval from 30 min to 2 hours.

The intensity of the main peak at 31.5° in the four diffractograms increases significantly as in Fig. 2 d (2 hours of mechanochemical activation) we have an intense peak in contrast with fig. 3 a) activation after 30 minutes. A decrease in the crystallite size from 118 nm to 20 nm of the target phase BaTiO₃ was found. At 28°, a glass-ceramic phase Bi₁₂TiO₂₀ is formed.

After the analysis of the obtained experimental data, as a main recommendation for the purpose of a more efficient and complete course of the reaction processes, synthesis of a monophasic end product and the absence of residual amounts of starting reagents, it can be recommended to further increase the period of mechanochemical treatment by 1-2 hours. Such a partial change of the used technological mode is perceived as more expedient and cost-effective than applying an increase in the temperature of maximum heat treatment and the time of isothermal loading.

The study of phase transformations in different oxide systems subjected to mechanochemical treatment is not only of fundamental scientific interest, but is related to the development of innovative technological solutions potentially applicable in practice. Obtaining different products at lower temperatures than those required for classic high-temperature syntheses would significantly ease the technological process and reduce costs related to the need for appropriate equipment, inevitable depreciation of equipment and increased consumption of energy carriers.

4. Conclusion

The participation of bismuth in the starting products for synthesis contributes to a more complete preparation of barium titanate as a final product. By applying prolonged mechanochemical activation, the degree of homogenization of the prepared batches increases significantly, the contact active surface of the introduced reagents increases, the crystallite sizes decrease, energetically excited states are formed, which determines the effective increase in the reactivity of the system and the lowering of the temperature values necessary for phase synthesis. The synthesized titanate phase is potentially applicable in practice in the form of nanosized powdered products with high specific surfaces or molded monolithic products prepared by applying appropriate technological methods. Another current possibility is the deposition of the obtained phase in the role of thin films, single-layer or multi-layer coatings on metal surfaces and the preparation of details with a variety of functional purposes.

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