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Synthesis of BaTiO₃ from a Mechanically Activated BaCO₃-TiO₂ System

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Abstract:

In this article the solid state reaction of BaTiO₃ formation from a mechanically activated BaCO₃-TiO₂ system has been investigated. An equimolar mixture of BaCO₃ and TiO₂ powders was activated in a planetary ball mill in a continual regime for 0, 30 and 90 min, pressed and thermally treated up to 1200°C. The effect of the milling and firing regime on the phase formation was investigated by the X-ray diffraction (XRD) method and differential thermal analysis (DTA). Deconvolution of the experimental DTA curve corresponding to the BaTiO₃ synthesis process has been performed. The influence of the activation time on the change of characteristic temperature for each elementary step in the complete solid-state reaction of BaTiO₃ formation, was analyzed. These results were correlated with the ones obtained by SEM characterization and by XRD analysis.

Keywords: Barium titanate, Mechanical activation, Sintering.

Introduction

It is well known that barium titanate based materials are widely used in the electroceramic industry [1]. Conventional processing of these materials mostly relies on high temperature solid state reactions between mixed oxides. In order to produce better quality of initial powder, numerous factors, such as the quality of raw materials, granulometry, mixture homogeneity, nature of reaction atmosphere etc. have to be controlled [2]. Thus, many processing routes including sol-gel synthesis, coprecipitation methods and mechanical activation have been developed [3-5]. Initially, mechanical activation was developed for the synthesis of intermetallics and alloy compounds and later it has been applied to improve the reactivity of the starting composition, so that the ceramic phase transformation is formed at reduced calcination temperature [6]. Several investigations have been carried out in order to obtain BaTiO₃ by mechanically activating the reactants [7-9]. Our earlier studies emphasized that mechanical activation of the BaCO₃-TiO₂ mixture in a high energy vibromill led to the formation of a desired ceramic phase at a reduced calcination temperature [8]. Significant influence of the milling regime on the mean crystallite size and crystal lattice microstrains into obtained BaTiO₃ powders was also determined [9]. C.Gomez-Yanez et al. reported that

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long term milling of a BaCO₃-TiO₂ mixture in an attritor has provoked the remaining of a large orthotitanate phase amount even after post-annealing at 1200°C during 1h, mainly due to previous particle agglomeration and the production of rather large and well defined Ba₂TiO₄ crystals during milling [10]. On the other hand, E. Brzozowski et al. brought into evidence a significant influence of long term milling on the agglomeration of TiO₂ small particles and the generation of Ti-rich phases, in the case when the BaCO₃/TiO₂ ratio differed from 1:1 [11]. In general, among various examinations of the influence of milling on BaTiO₃ formation by annealing of BaCO₃-TiO₂ mixtures, some indications seem quite contradictory, especially considering the results of DTA research [10-11]. Having all this in mind, in this paper the influence of the mechanically enhanced reactivity of the raw materials (BaCO₃-TiO₂) on the kinetics of BaTiO₃ synthesis, as well as on the microstructure characteristics, has been reported. Reaction kinetics and mechanism of BaTiO₃ formation has been analyzed by deconvolution of the corresponding DTA-experimental curve, as well as by XRD examinations.

Experimental

A mixture with equal molar ratio of commercially available BaCO₃ (Merck, p.a. 99%) and TiO₂ (Ventron, p.a. 99,8%) powders was used as the starting material. Mechanical activation was performed in a planetary-ball mill (Fritsch Pulverisette 5), for durations up to 90 min, in an agate jar with agate balls (8mm in diameter), with the tray and vial rotation speeds of 317 and 396 rpm, respectively. The ball/sample mass ratio was 20:1. Mechanically activated equimolar mixtures of BaCO₃ and TiO₂ powders were thermally treated up to 1200°C with a heating rate of 10°C/min.

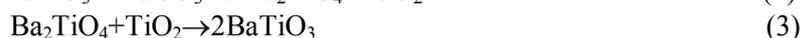
The effect of the milling and firing regime on the phase formation was investigated by the X-ray diffraction method (XRD) and differential thermal analysis (DTA). X-ray diffraction patterns were obtained using a PHILIPS PW-1820 diffractometer with CuKα_{1/2} radiation, graphite monochromator and step-scanning mode (0.02°/20s), while differential thermal analysis was conducted in a DTA-50 Shimadzu, with a heating rate of 10°C/min.

Microstructure characterization of the mixtures and calcinated samples was carried out using a JEOL-JSM-T20 scanning electron microscope.

Results and discussion

High energy mechanical milling proved to be an effective method that can modify the processing conditions of desired ceramic phase formation due to energetic and structural changes in reactants. Our investigations pointed out that mechanical activation strongly affected the lowering of the temperature of BaTiO₃ formation free of second phases, including lowering of the starting reaction temperature. XRD examinations of fired and air-quenched samples indicated that BaTiO₃ synthesis from a mechanically activated BaCO₃-TiO₂ mixture proceeded via formation of Ba₂TiO₄ as an intermediate phase (Fig.1). These results are in accordance with the observations of Brzozowski et al. [11] and Cheung et al. [12] and can be explained by the higher reactivity of longer milled mixtures.

According to the obtained diffractograms, the three elementary steps of a complete solid-state reaction of BaTiO₃ formation were assumed:



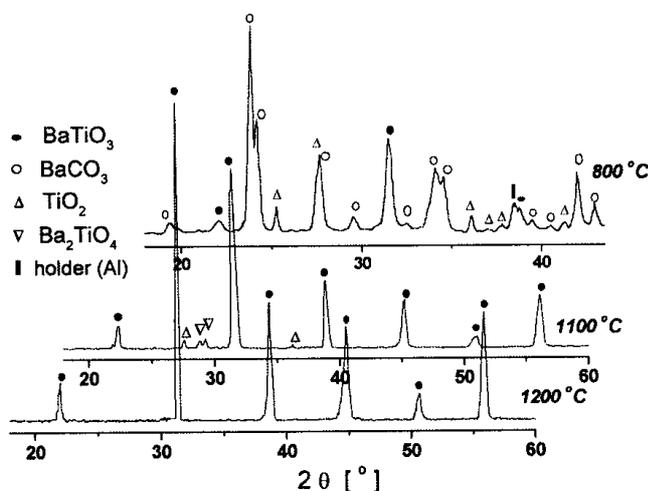


Fig. 1 X-ray diffraction patterns of the fired samples obtained from the $\text{BaCO}_3\text{-TiO}_2$ mixture activated for 90 min

DTA examinations confirmed the significant influence of the milling time on lowering of the BaTiO_3 formation temperature. Thermal events detected by DTA for the nonactivated and mechanically activated starting mixtures are shown in Fig. 2. The first peak indicates the polymorph transition from γ - to β - BaCO_3 form. The main peak, a rather large and broad DTA event, can be related to the solid-state reaction of BaTiO_3 synthesis.

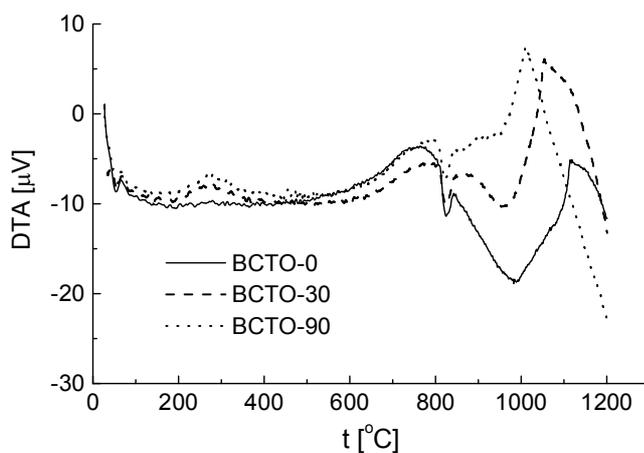


Fig. 2 DTA curves of a mechanically activated $\text{BaCO}_3\text{-TiO}_2$ system

It can be seen that more rigorous milling changes the shape and the position of the solid-state reaction peak. The weak overlapping of the two obtained thermal events is in accordance with our previous XRD results of fired activated mixtures (180 min of activation) which showed the appearing of certain amounts of BaTiO_3 cubic phase even at 800°C [8]. An asymmetrical shape of the large peak in the DTA curve indicates that the formation of BaTiO_3 can be analyzed as a multi-step reaction. In order to perform deconvolution of the DTA event attributed to the BaTiO_3 synthesis for different activation times, a fitting method via several analytical profiles was carried out. Experimental profiles were fitted with the functions which could be presented as combinations of several Gaussians, as well as the summary of Lorentzian type profile functions. The best fit, considering the minimum of standard deviation values, was obtained using the function defined as:

$$y = y_0 + \sum_{i=1}^3 a_i \exp\left(-0.5\left(\frac{x-b_i}{c_i}\right)^2\right) \quad (4)$$

where y_0 , a , b and c represent the fitting parameters. The presented fitting process, via a summary of the three equal function types, reflects the fact that all the assumed steps of BaTiO₃ synthesis (according to eq. 1, 2 and 3) represent the same process type that belongs to the topochemical heterogeneous solid-state reaction of synthesis. Very good matching of experimental and fitting curves is noticeable (Fig. 3).

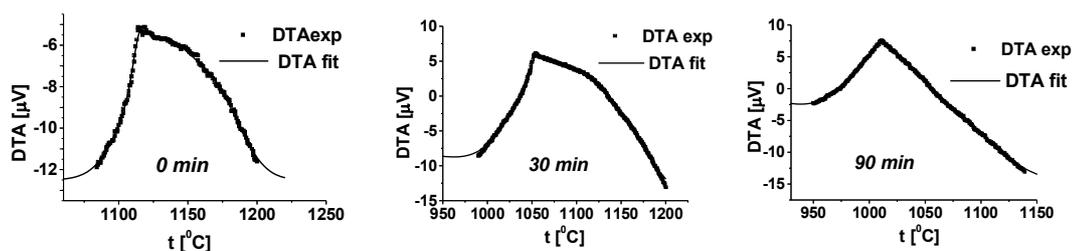


Fig. 3 Matching between fitted and experimental curves

Fitting results and the values of the correlation fitting parameter, which indicates a matching degree are displayed in Tab.I. A significant influence of mechanical activation on lowering the temperature t_m , which is characteristic for each elementary step in the complete solid-state reaction of BaTiO₃ formation can be noticed.

Tab. I. Correlation parameters and characteristic temperatures of each elementary process for different regimes of mechanical activation

t_A [s]	$r^2_{\text{Coef.Det.}}$	t_m [°C]		
		I	II	III
0	0.996	1115	1126	1167
30	0.997	1054	1067	1137
90	0.999	1010	1018	1085

For the first-step reaction (eq. 1), decreasing of t_m with the increase of activation time is the consequence of increase of the specific surface area and the total free (Gibbs) energy of the disperse BaCO₃-TiO₂ system and the increase of structural defect concentration in the near surface layers, which is accompanied with a lowering of the potential barrier for a new phase nucleation process.

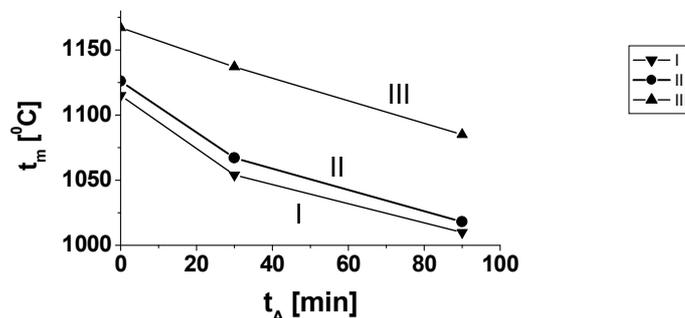


Fig. 4 Dependence of the characteristic temperature t_m v.s. activation time t_A

However, the lowering of t_m is less perceptible for the increase of the activation time from 30 min to 90 min than for the increase up to 30 min (Fig. 4). According to our SEM investigations of the sintered materials, this is probably due to increase of secondary agglomeration within the samples activated for 90 min. (Fig. 5).

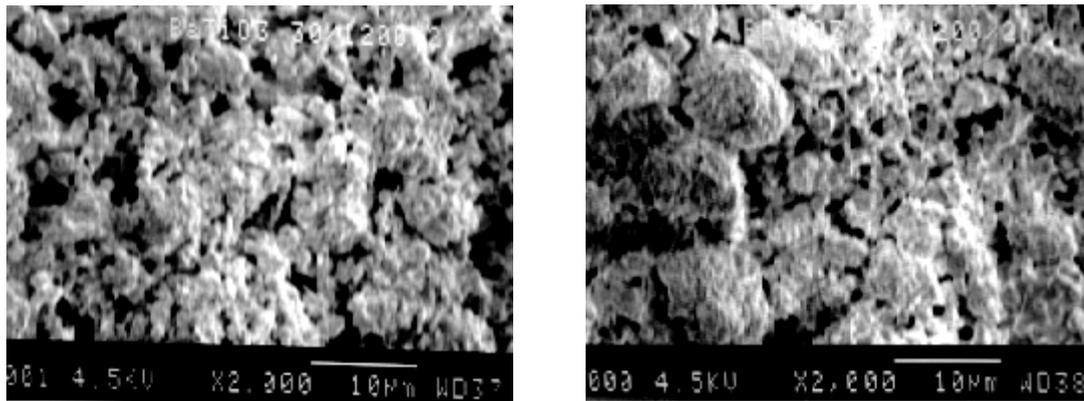


Fig. 5 Microstructures of samples sintered at 1200°C and activated for: a) 30 min. b) 90 min

The beginning and developing of the second-step reaction (eq. 2) seems to be appreciably influenced by a primarily formed $BaTiO_3$ layer around the TiO_2 particles. Since it has been experimentally confirmed that activation of the starting powders lowers the initial first-step reaction temperature, it can be deduced that mechanical activation led to the formation of a $BaTiO_3$ layer at lower temperatures. Hence, the second-step reaction will begin and will attain the maximal rate at lower temperatures in the case of longer milling of the starting mixtures. On the other hand, there is also a deterioration effect of the secondary agglomeration on the initially second-stage reaction temperature, as well as on the t_m .

Since the diminution of the mean particle diameter in the starting mixtures is one of the most dominant consequence of the milling process, mechanical activation will lead to shorter diffusion paths of ions through the reactants and product layers. According to this, the ions diffusion paths through the $BaTiO_3$ layer between TiO_2 and Ba_2TiO_4 phases are very important parameters for development of the third-step reaction. The increase of activation time will lower the temperature at which diffusion effects will enable the beginning and further proceeding of the third-step reaction. This implies the lowering of temperature t_m for the mentioned reaction step. An undesirable effect of secondary agglomeration is not distinct (Tab.I, Fig.4) but rather covered within: a) the influence of the temperature lowering of maximal second-step reaction rate and b) a diminution particle size-effect.

It is important to notice that the presented lowering of t_m for each of the three assumed elementary steps in the $BaTiO_3$ formation process also indicates the influence of mechanical activation on the shift of the other t_m -related parameters values such as: the pick-corresponding rate and the extent of reaction, activation energy, pre-exponential factor in Arrhenius equation, etc [13].

Conclusions

In this paper synthesis of $BaTiO_3$ from mechanically activated $BaCO_3$ - TiO_2 mixtures has been studied. The contribution of mechanical activation to the kinetics of $BaTiO_3$ formation has been analyzed. DTA examinations, as well as XRD results, have confirmed a significant influence of the milling time on lowering the temperature of $BaTiO_3$ formation free of second phases. In order to perform a deconvolution of the asymmetric DTA event

obtained for the BaTiO₃ synthesis process for various activation times, a fitting method via several analytical profiles was carried out. Very good matching of the experimental and fitting curves for different activation times was achieved. The influence of the activation time on the change of the characteristic temperature for each elementary step in the complete solid-state reaction of the BaTiO₃ formation, was analyzed.

Acknowledgements

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References

1. L.E.Cross, Am.Ceram.Soc.Bull. 63 (1984) 586.
2. A.Amin, M.A.Spears, B.Kulwicki, J.Am.Ceram.Soc. 66 (1983) 733.
3. G.Pfaf, J.Mater. Chem. 2 (1992) 591.
4. F.S.Yen, C.T.Chang, Y.H.Chang, J.Am.Ceram.Soc. 73 (1990) 3422.
5. O.Abe, Y.Suzuki, Mat.Sci.Forum 225 (1996) 563.
6. Zhang D.L., Progress in Materials Science 49 (2004) 537.
7. J.Xue, J.Wang, D.Wan, J.Am.Ceram.Soc. 1 (2000) 83.
8. V. P. Pavlović, B. D. Stojanović, V. B. Pavlović, Lj. Zivković, M. M. Ristić, Sci. Sint. 34 (2002) 73.
9. B.A.Marinković, B.D.Stojanović, V.B.Pavlović, V.P.Pavlović, M.M.Ristić, Mat. Struct. 6 (1999) 96.
10. V.Berbenni, A.Marini, G.Bruni Thermochemica Acta 374 (2001) 151.
11. C.Gomez-Yanez, C.Benitez, H.Balmori-Ramirez, Cer. International 26 (2000) 271.
12. E. Brzozowski, M.S.Castro, Thermochemica Acta 398 (2003) 123.
13. M.C.Cheung, H.L.Chan, C.L.Chou, J.Mat.Sci. 36 (2001) 381.
14. D.Dollimore, P.Tong, K.Alexander, Thermochemica Acta 282/283 (1996) 13.

Садржај: У овој раду је анализиран утицај механичке активације система BaCO₃-TiO₂ на формирање BaTiO₃. Еквимоларне мешаве праха BaCO₃ и TiO₂ су активирани у планетарном млину у континуалном режиму током 0, 30 и 90 min. Узорци су затим пресовани и термички третирани до 1200°C. Ефекат млевења и загревања на промене фаза је анализиран применом рендгенске фазне анализе и диференцијалне термијске анализе. Извршена је деконволуција експериментално добијене ДТА криве која одговара процесу синтезе BaTiO₃, као и анализа утицаја времена активације на промене карактеристичне температуре за сваки појединачни елементарни процес током синтезе баријум титаната. Ови резултати су корелисани са резултатима добијеним SEM и XRD анализом.

Кључне речи: Баријум титанат, механичка активација, синтеровање.
