Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 1017–1021

Short Communications

THERMAL PROPERTIES OF MECHANOCHEMICALLY PRETREATED PRECURSORS OF $BaTiO_3$ SYNTHESIS

P. Baláz[1] *and B. Plešingerová*[2]

[1]Institute of Geotechnics, Slovak Academy of Sciences, 043 53 Košice
[2]Faculty of Metallurgy, Technical University, 043 85 Košice, Slovakia

(Received April 18, 1999)

Abstract

The changes of physico-chemical properties of mechanochemically pretreated ($BaCO_3$+TiO_2+PbO) powders were investigated. The values of apparent activation energy of $BaTiO_3$ formation calculated by the Freeman and Carroll method decrease with milling time. The changes of precursors density may be interpreted as a consequence of mechanochemical reactions during milling.

Keywords: barium titanate, density, DTA, mechanochemistry, TG

Introduction

$BaTiO_3$ powders modified with dopants belong to materials with a positive temperature coefficient of resistance. These powders are traditionally prepared by solid-state reactions between barium carbonate or oxide, TiO_2 and dopants at temperatures above 1000°C [1–3].

There are several possibilities of influencing the properties of the arising solid-phase product. One of them is the mechanochemical pretreatment of the precursors by high-energy milling [4–8]. In our preceding study [9] we investigated the influence of milling of the precursors of high-temperature synthesis of $BaTiO_3$ on XPS properties and the morphology of synthetized particles.

The aim of this study was to obtain information about thermal properties and density of mechanochemically pretreated ($BaCO_3$+TiO_2+PbO) powders which are the precursors of doped $BaTiO_3$ ceramics.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

The investigations were carried out with chemically pure substances, i.e. $BaCO_3$ (for ferroelectrics), TiO_2 anatase (for ferroelectrics) and PbO yellow. All chemicals were the products of Lachema (Czech Republic). Before the experiments a mixture with molar ratio $BaCO_3$:TiO_2:PbO = 1.00:1.15:0.10 was homogenized by stirring in methanol for 60 min.

The homogenized samples (20 g each) 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 activation: 30–240 min in methanol (35 ml); relative acceleration of the mill: b/g=12.4.

The specific surface area S_A was determined by the low-temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

Combined TG-DTA measurements were carried out on a thermoanalyser Mac Science working in the following mode of operation: sample mass, 30 mg; temperature range 293–1372 K, air flow-rate 200 ml min^{-1}, linear rate of heating 6 K min^{-1}.

The activation energy of the $BaTiO_3$ formation was calculated from TG data by using the Freeman and Carroll method [10].

Results and discussion

The properties of mechanically activated mixture of the precursors ($BaCO_3$+TiO_2+PbO) of high-temperature synthesis of $BaTiO_3$ were investigated by the methods of thermal analysis. In Fig. 1 the TG-DTA record obtained for the mixture activated by milling for 30 min is represented (note: the records obtained for other milling times are qualitatively similar). The TG curve (1) shows gradual decrease in mass of the sample up to 1073 K where this decrease becomes considerably marked. On the DTA curve (2) we can identify three endoeffects at characteristic temperatures of 572, 1097 and 1190 K. The effect with the maximum at 572 K may be due to the decomposition of $Ba(OH)_2$. This compound is formed by hydration of BaO which is a product of partial decarbonization of $BaCO_3$ during milling. The effect at 1097 K corresponds to phase transformation

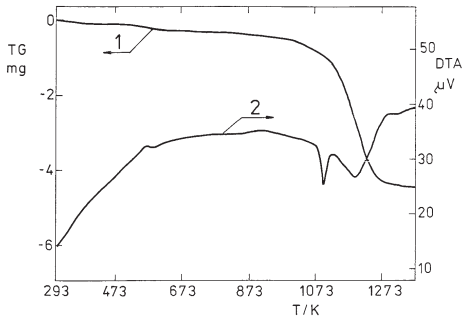

Fig. 1 TG-DTA record for sample activated 30 min

α-$BaCO_3 \rightarrow \beta$-$BaCO_3$ [11]. It is overlapped by the most conspicuous endoeffect on the DTA curve at 1190 K and accompanied by a considerable decrease in mass of sample. This decrease is due to the liberation of carbon dioxide arising in high-temperature synthesis of $BaTiO_3$ according to equation

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \quad (1)$$

The initial temperature of the endoeffect discussed appears at about 873 K which is in good agreement with the statement of Tagawa [1] who the attributes the initial temperature of 893 K to reaction (1).

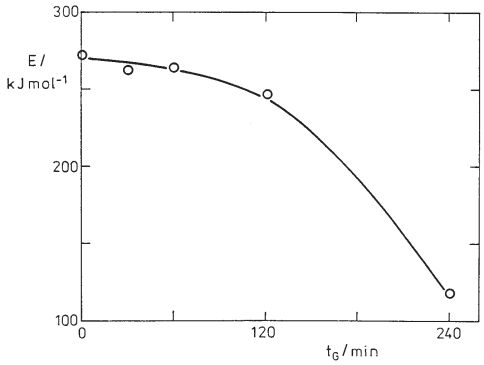

Fig. 2 Dependence of experimental activation energy of $BaTiO_3$ formation on activation time t_G

The values of apparent activation energy of $BaTiO_3$ formation calculated from the TG data are plotted in Fig. 2 as a function of milling time. In general, we can state that the activation energy of the process of high-temperature synthesis decreases with milling. According to Karagedov [12] the intensive milling of titanium dioxide and barium carbonate results in formation of particle aggregates owing to which the indi-

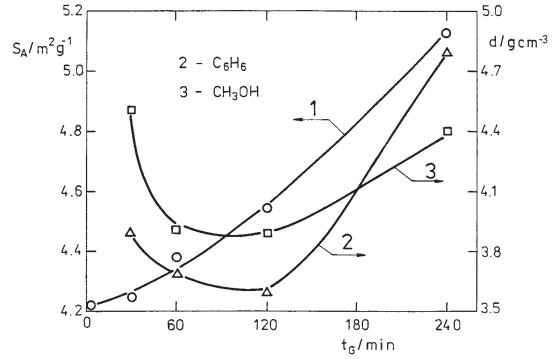

Fig. 3 Variation of specific adsorption surface S_A (1) and density d (2, 3) with activation time t_G, media applied by measuring the density: 2 – C_6H_6; 3 – CH_3OH

vidual precursors of the solid-phase reaction come in more closer mutual contacts. This fact promotes the following thermal reaction because the diffusion paths of reaction substances are shortened and the interfacial reaction surface is increased. These facts bring about a decrease in activation energy of solid state reaction (1).

According to the course of the specific surface of the precursors mixture (Fig. 3, curve 1) we can state that this parameter increases with activation time in the whole investigated interval. It is likely that the increase in surface results in an increase in number of contact points of reacting particles and the reaction exhibits lower activation energy.

The course of density of reacting particles measured in two media – benzene (Fig. 3, curve 2) and methanol (Fig. 3, curve 3) is similar. The differences are due to different densities of the used liquid medium. The values decrease with the activation time up to 120 min. This effect is to be unambiguously incident to particle disintegration during grinding. However, the course of density values at t_G>120 min shows the opposite tendency. The increase observed could be explained by particle compaction, nevertheless only in case of their specific surface is subject to stagnation or reduction. However, in our case the surface increases and that is why we can assume the existence of mechanochemical reaction. The interpretation is not unambiguous. It may be a case of $BaCO_3$ decarbonization in mill and subsequent hydration of BaO to $Ba(OH)_2$ as we have discovered in our preceding work by investigating the XPS properties of these samples [9]. The second possibility of explaining the increase in density values may proceed from the beginning phase transformation anatase→rutile taking place in the course of long-term grinding. Avvakumov [13] has found that the phase transformation of these TiO_2 forms is accompanied by a density increase just as a result of rutile origination.

The changes in properties of the precursors of high-temperature $BaTiO_3$ synthesis indicate the fact that besides the favourable homogenization effect milling may also produce other effects which ought to be identified.

* * *

The authors wish to express their thanks to Prof. M. Senna of Keio University (Yokohama) for his help by measuring of thermoanalytic data. This work was partly supported (P.B.) by the Slovak Grant Agency for Science VEGA (grant No. 2/6101/99).

References

1 H. Tagawa and J. Ohashi, J. Electrochem. Soc. Japan, 52 (1984) 485.
2 G. Pfaff, Z. Chem., 28 (1988) 76.
3 G. Pfaff, Cryst. Res. Technol., 26 (1991) 305.
4 T. Yamaguchi, S.H. Cho, H. Nagai and H. Kuno, in 'Reactivity of Solids', Proc. 8th Int. Symp., Göteborg 1976 (J. Wood, O. Lindqvist, C. Helgesson, N.G. Vannerberg, eds.), Plenum, New York 1977, p. 701.
5 G. Heinicke, Tribochemistry, Akademie Verlag, Berlin 1984, p. 495.
6 W. F. Kladnik, Int. Ceramic Review, 39 (1990) 1.

7 M. Drofenik, J. Am. Ceram. Soc., 75 (1992) 2383.
8 J. G. Baek, K. Gomi, T. Watanabe, T. Isobe and M. Senna, Materials Science Forum, 235–238 (1997) 115.
9 P. Baláz, J. Briančin, Z. Bastl, Ľ. Medvecký and V. Šepelák, J. Mat. Science, 29 (1994) 4847.
10 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
11 A. Blazek, Thermal Analysis, SNTL, Prague 1972, p. 294 (in Czech).
12 G. R. Karagedov, in 'InCoMe '93', Proc. Ist Int. Conf. on Mechanochemistry, Košice 1993, (K. Tkáčová et al., ed.), Cambridge Interscience Publishing, Cambridge 1994, p. 94.
13 E. G. Avvakumov, Mechanical Methods of Chemical Processes Activation, Nauka, Novosibirsk 1986, p. 303 (in Russian).