

STUDY OF SYNTHESIS AND MORPHOLOGY OF BaTiO<sub>3</sub> CRYSTALS PREPARED FROM MOLTEN SALTS

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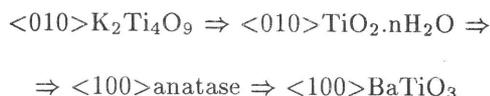
*The synthesis of barium-titanium mixed oxide, BaTiO<sub>3</sub>, from the mixture of barium sulphate, sodium carbonate and titanium oxide in the medium of the molten alkali metal chlorides was realized at the temperatures of 700–900 °C and reaction times of 1–30 min. The conversion degree increases both with temperature and time of heating and in the presence of flux attains at 900 °C almost 100%. The synthesized powders contained BaTiO<sub>3</sub> crystals of two different morphology. The equiaxed BaTiO<sub>3</sub> crystals originate most probably by disintegration of the primarily formed rod-like crystals. According to the X-ray diffraction analysis all prepared powders contain only the tetragonal modification of BaTiO<sub>3</sub>. The activation energy of the BaTiO<sub>3</sub> formation was found to be  $\Delta E(\text{BaTiO}_3) = 124.6 \text{ kJ/mol}$ .*

## INTRODUCTION

The solid state preparation of well defined mixed oxide BaTiO<sub>3</sub> powder is relatively pretentious because of possible side products, high energy and time consumption and hard control of the particle shape and dispersity [1]. Well dispersed powders of BaTiO<sub>3</sub> mixed oxide may be prepared with advantage by precipitation in molten salt medium [2, 3]. In [3] it was found that the BaTiO<sub>3</sub> powder prepared from the mixture of BaCO<sub>3</sub> and rod-like potassium tetratitanate, TiO<sub>2</sub>·nH<sub>2</sub>O, or anatase particles, respectively, in the NaCl – KCl melt contained in all cases both rod-like and equiaxed BaTiO<sub>3</sub> crystals. The authors of [3] assumed that the BaTiO<sub>3</sub> formation takes place by a topotactic reactions since the rod-like BaTiO<sub>3</sub> particles retain the similar shape of the titanium-source particles. The formation of the equiaxed crystals may be due to three possible mechanisms

- (i) the disintegration of the rod-like titanium source particles before reacting with BaCO<sub>3</sub>,
- (ii) the dissolution of reactant particles and precipitation of BaTiO<sub>3</sub>,
- (iii) the disintegration of the already formed BaTiO<sub>3</sub> rod-like particles.

The formation mechanism of rod-like BaTiO<sub>3</sub> particles was elucidated by means of the X-ray powder and electron diffraction analysis as well as the transmission electron microscopic study. The following topotactic relation was assumed [3]

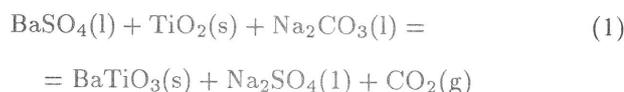


In the present work the attempt was made to prepare BaTiO<sub>3</sub> powders from other starting sources to obtain uniform isometric BaTiO<sub>3</sub> particles. Thus the

morphology of BaTiO<sub>3</sub> prepared by reaction of the equiaxed anatase crystals with barium sulfate and sodium carbonate in the medium of molten alkali metal chlorides was studied. The promoting effect of the liquid phase on the reaction kinetics was evaluated by comparison with the solid state reaction.

## EXPERIMENTAL

For the preparation of the barium-titanium mixed oxide BaTiO<sub>3</sub> the following reagents were used: polycrystalline anatase, the diameter of the spherical particles was 1–5 μm (see Fig. 1), and reagent grade barium sulfate and sodium carbonate. Sodium chloride at the temperature of 900 °C, potassium chloride at 800 °C and the equimolar mixture NaCl – KCl at 700 °C were used as flux. The reaction times chosen were in the interval from 1 to 30 min. The total chemical reaction of the BaTiO<sub>3</sub> formation was



The mixtures were heated in platinum crucibles at the desired temperature. After heating for the desired time the samples were quenched in distilled water. The flux was dissolved in boiling water. The insoluble products were several times washed, dried and analysed. The preparation procedure was described in detail in our previous work [4].

The morphology of the powder products were examined by means of the scanning electron microscope JEOL X5C. The average diameter of the BaTiO<sub>3</sub> particles was not determined since due to the very high aspect ratio of the rod-like ones it was not possible to estimate their actual particle length. The composition of the samples was determined using the X-ray powder diffraction analysis and X-ray electron microprobe JEOL YXA – 840A EDA – KEVEX. The

Table I.

The temperature dependence of the weight loss of the mixtures due to CO<sub>2</sub> escape. The values refer to the percentage of the total CO<sub>2</sub> loss at the heating rate of 10 °C/min.

$t$ °C	$\frac{\text{BaCO}_3 + \text{TiO}_2}{\text{mass \%}}$	$\frac{\text{BaSO}_4 + \text{Na}_2\text{CO}_3 + \text{TiO}_2}{\text{mass \%}}$
100	0.5	2.0
200	3.5	6.0
300	5.5	8.5
400	6.5	9.5
500	7.5	10.7
600	9.0	15.5
700	12.5	45.5
800	18.5	71.0
900	28.0	79.0
1000	52.0	83.5

degree of conversion of the reaction (1) was also determined using the thermogravimetric analysis by measurement of the weight loss due to the CO<sub>2</sub> escape. The evaporation of the melt was neglected. The measurements were carried out at normal pressure, so the dependence of the conversion degree on the CO<sub>2</sub> pressure was not considered.

## RESULTS AND DISCUSSION

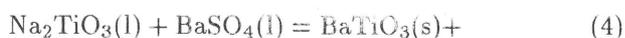
The temperature dependences of the weight loss of the BaCO<sub>3</sub> + TiO<sub>2</sub> mixture by solid state reaction and the BaSO<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub> + TiO<sub>2</sub> mixture in molten salt medium due to the CO<sub>2</sub> escape during the BaTiO<sub>3</sub> formation are summarized in Table I. The results confirm the fact that the formation of BaTiO<sub>3</sub> in the molten salts is more intensive than that in the solid state. From the X-ray phase analysis it follows, that like in the case of SrTiO<sub>3</sub> [5], the formation of BaTiO<sub>3</sub> takes place through the primary formation of the intermediate product of sodium-titanium mixed oxide. This conclusion is supported also by the values of the Gibbs energy of the BaTiO<sub>3</sub> and Na<sub>2</sub>TiO<sub>3</sub> formation, respectively, according to the reactions [6]



$$\Delta G^0(1000\text{K}) = 133.9 \text{ kJ}$$



$$\Delta G^0(1000\text{K}) = -11.2 \text{ kJ}$$



$$\Delta G^0(1000\text{K}) = -23.5 \text{ kJ}$$

It was confirmed that like in the previous work [3], the BaTiO<sub>3</sub> crystals originated at the given conditions in two different morphologic forms. The microphotographs of the BaTiO<sub>3</sub> crystals prepared at different conditions in the molten alkali metal chlorides medium are shown in Figs. 2a, b to 5a, b. From the microphotographs it follows that at all chosen temperatures and reaction times the obtained powders contain both the rod-like and equiaxed crystalline forms. Because the equiaxed polycrystalline anatase served as the titanium source, it may be concluded that the morphologic form of the originated BaTiO<sub>3</sub> particles does not depend on the shape of the starting material.

By the X-ray electron microanalysis of selected rod-like and equiaxed crystals it was found that in both cases the composition relates to BaTiO<sub>3</sub>. The determined content of Ba and Ti expressed in atomic % was 51.2% Ti and 48.8% Ba in the rod-like crystals and 48.2% Ti and 51.8% Ba in the equiaxed crystals. The uncertainty in the composition may be ascribed either to the error in the composition determination or to the contamination of BaTiO<sub>3</sub> with the by-products.

The X-ray diffraction patterns of all prepared powders were identical with the published diffraction patterns for the tetragonal modification of BaTiO<sub>3</sub>, which indicates that both the rod-like and equiaxed forms are crystallographically identical and refer to the tetragonal modification of BaTiO<sub>3</sub>. Unfortunately, it did not succeed to prepare a BaTiO<sub>3</sub> powder containing solely rod-like or equiaxed crystals. In fact, both the crystallographic forms, cubic and tetragonal, are hardly distinguishable since the parameters of the unit cell of the tetragonal form are very close ( $a = 0.3994 \text{ nm}$ ,  $c = 0.4038 \text{ nm}$ ) to that of the cubic form ( $a = 0.397 \text{ nm}$ ).

The results of the BaTiO<sub>3</sub> crystal formation study in the investigated time and temperature intervals indicate, that BaTiO<sub>3</sub> originates primarily in the rod-like form. The equiaxed crystals originate secondarily by disintegration of the rod-like ones at cooling from the reaction to the ambient temperature. This assumption supports the comparison of the microphotograph of BaTiO<sub>3</sub> powder prepared at the temperature of 900 °C and quenched (Fig. 5b) with that subsequently tempered for 4 h at the temperature of 300 °C and then slowly cooled (approx. 1 °C/min) to the ambient temperature (Fig. 6). From Fig. 6 it follows that the rod-like crystals break up to the equiaxed ones. It may be therefore concluded that the rod-like BaTiO<sub>3</sub> crystals are the primary product of the precipitation in molten salts. The equiaxed crystals originate secondarily by disintegration of the former ones. The opposite process i.e. the sintering of

equiaxed crystals to form rod-like ones seems to be very unlikely.

The time and temperature dependence of the conversion degree of TiO<sub>2</sub> to the mixed oxide BaTiO<sub>3</sub> was determined by means of the semiquantitative X-ray phase analysis. The intensities of the tetragonal BaTiO<sub>3</sub> diffraction lines at 0.230 and 0.399 nm were measured for the analysis. The determined values of the conversion degree at the temperatures of 700, 800 and 900 °C in dependence on the reaction time are summarized in Table 2.

Table II.

The dependence of the conversion degree of TiO<sub>2</sub> to BaTiO<sub>3</sub> on the exposure time at the temperatures of 700, 800 and 900 °C.

700 °C		800 °C		900 °C	
<i>t/s</i>	$\alpha$	<i>t/s</i>	$\alpha$	<i>t/s</i>	$\alpha$
66	0.0	72	0.27	68	0.49
128	0.10	140	0.36	126	0.55
302	0.18	308	0.53	302	0.65
605	0.33	620	0.62	650	0.74
1200	0.48	1230	0.80	1200	0.90
1820	0.55	1900	0.83	1820	0.95

The determined dependences were used for the calculation of the time needed for attaining the same conversion degree at different temperatures to calculate the activation energy of the BaTiO<sub>3</sub> formation. The calculation was carried out using the equation [7]

$$\ln t(\alpha) = \frac{\Delta E}{RT} + \text{const.} \quad (5)$$

where  $t(\alpha)$  is the time needed for attaining the same conversion degree  $\alpha$  at different temperatures. It was supposed that at the given experimental conditions the activation energy of the process does not depend on temperature. The activation energy of the BaTiO<sub>3</sub> formation calculated in this manner has the value  $\Delta E = 124.6$  kJ/mol regardless of the conversion degree considered.

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### ŠTÚDIUM SYNTÉZY A MORFOLÓGIE KRYŠTÁLOV BaTiO<sub>3</sub> PRIPRAVENÝCH V PROSTREDÍ ROZTAVENÝCH SOLÍ

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Študovali sa podmienky syntézy podvojného oxidu titaničito bárnateho, BaTiO<sub>3</sub>, zo zmesi síranu bárnateho, uhličitanu sodného a oxidu titaničitého v prostredí roztavených chloridov alkalických kovov. Syntéza sa uskutočnila pri teplote 700–900 °C a reakčnom čase 1–30 min. Stupeň konverzie rástol s teplotou a časom tepelnej expozície, pri 900 °C dosahoval hodnotu 95%.

Syntetizovaný prášok obsahoval kryštály BaTiO<sub>3</sub> dvojakej morfológie. Izometrické kryštály BaTiO<sub>3</sub> vznikali rozpadom primárne vznikajúcich ihličkovitých kryštálov. Rtg difrakčnou analýzou sa zistilo, že pripravené prášky, ktoré boli zmesou ihličkovitých a izometrických kryštálov, obsahujú len tetragonálnu modifikáciu BaTiO<sub>3</sub>. Stanovila sa aktivačná energia tvorby BaTiO<sub>3</sub>  $\Delta E(\text{BaTiO}_3) = 124.6$  kJ/mol.

Obr. 1. Mikrofotografia východiskového polykryštalického anatasu použitého pri syntéze BaTiO<sub>3</sub>. Ukázaný je aj zväčšený povrch zrna.

Obr. 2. Mikrofotografia prášku BaTiO<sub>3</sub> pripraveného pri 700 °C a dobe záhrevu 66 s. a – ihličkovité kryštály, b – izometrické kryštály

Obr. 3. Mikrofotografia prášku BaTiO<sub>3</sub> pripraveného pri 700 °C a dobe záhrevu 1820 s. a – ihličkovité kryštály, b – izometrické kryštály

Obr. 4. Mikrofotografia prášku BaTiO<sub>3</sub> pripraveného pri 900 °C a dobe záhrevu 68 s. a – ihličkovité kryštály, b – izometrické kryštály

Obr. 5. Mikrofotografia prášku BaTiO<sub>3</sub> pripraveného pri 900 °C a dobe záhrevu 1820 s. a – ihličkovité kryštály, b – izometrické kryštály

Obr. 6. Mikrofotografia prášku BaTiO<sub>3</sub> temperovaného 4 h pri teplote 300 °C a následne pomaly chladeného na izbovú teplotu.

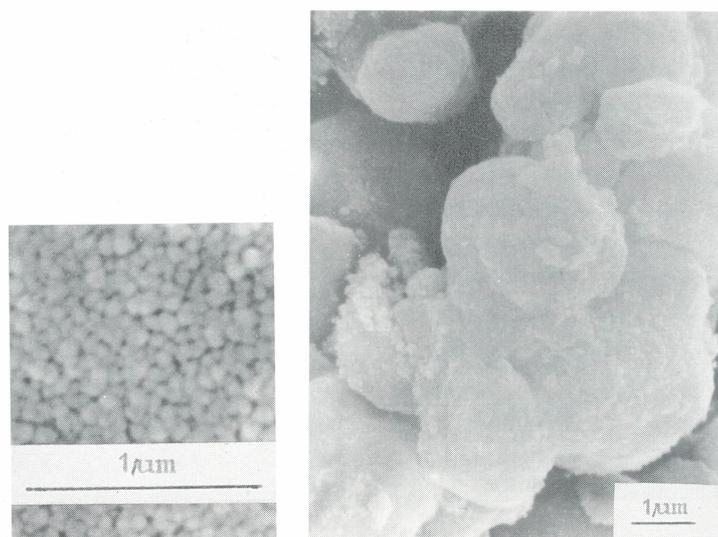


Fig. 1. Microphotograph of the starting polycrystalline anatase used in the BaTiO<sub>3</sub> synthesis. The enlarged surface of the individual grain is shown as well.

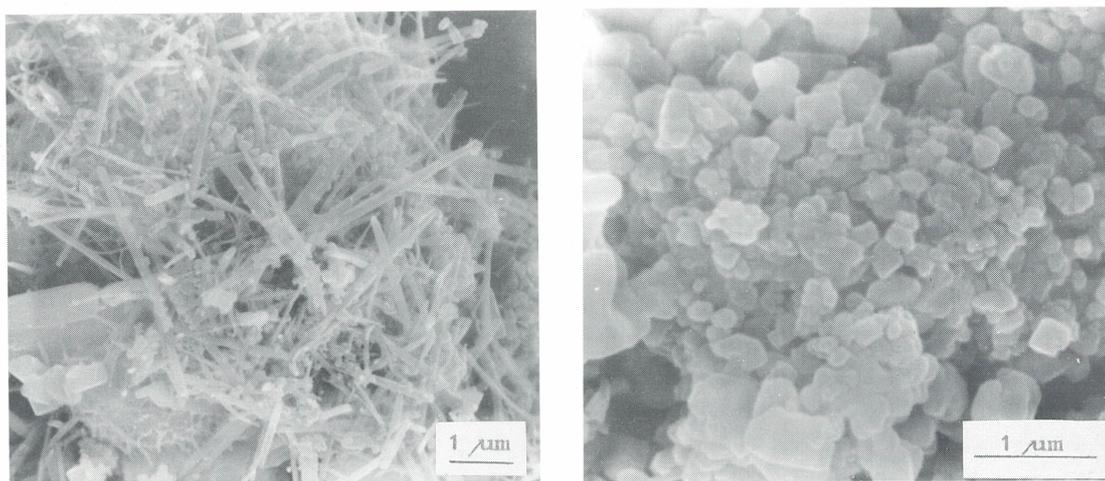


Fig. 2. Microphotographs of the prepared BaTiO<sub>3</sub> powder at 700 °C and the reaction time of 66 s. a - rod-like crystals, b - equiaxed crystals

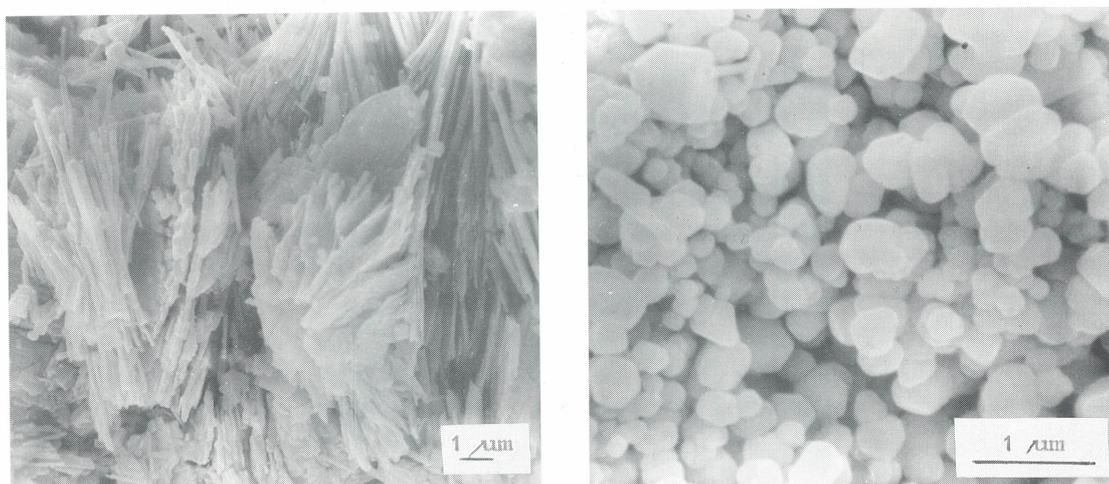


Fig. 3. Microphotographs of the prepared BaTiO<sub>3</sub> powder at 700 °C and the reaction time of 1820 s. a - rod-like crystals, b - equiaxed crystals

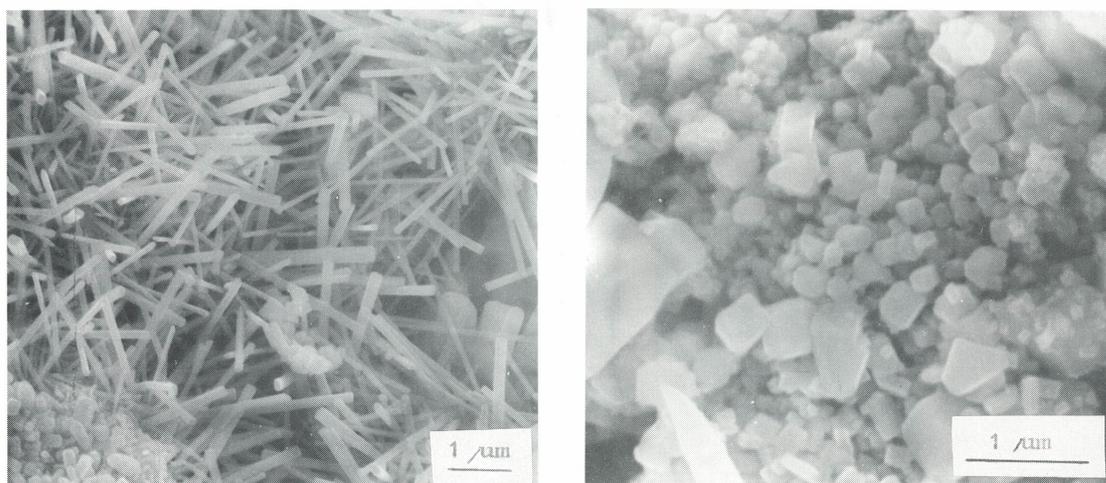


Fig. 4. Microphotographs of the prepared BaTiO<sub>3</sub> powder at 900 °C and the reaction time of 68 s. a – rod-like crystals, b – equiaxed crystals

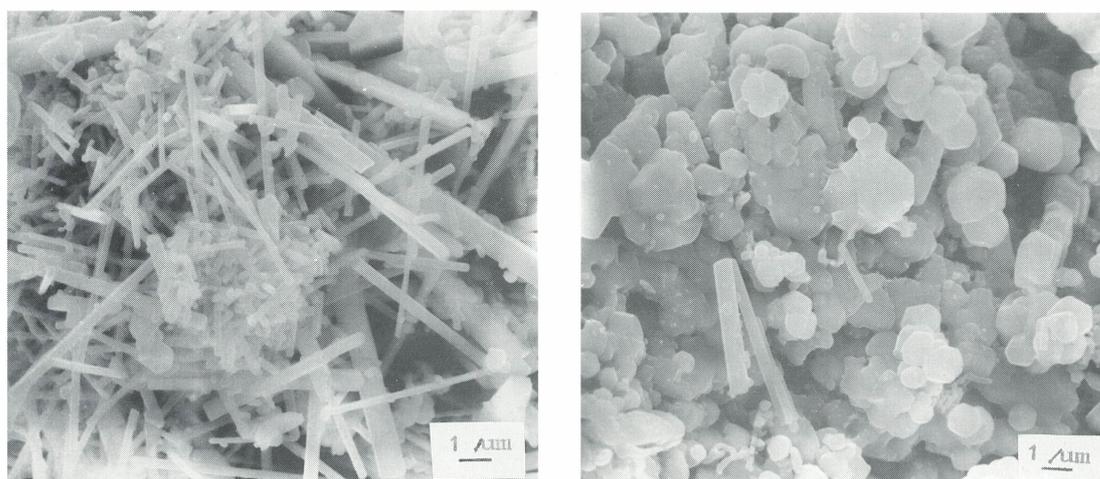


Fig. 5. Microphotographs of the prepared BaTiO<sub>3</sub> powder at 900 °C and the reaction time of 1820 s. a – rod-like crystals, b – equiaxed crystals

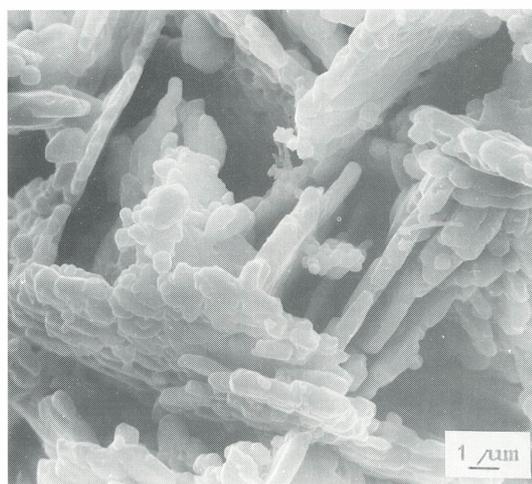


Fig. 6. Microphotograph of the BaTiO<sub>3</sub> powder tempered for 4 h at the temperature of 300 °C and subsequently slowly cooled to the ambient temperature.