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$BaTiO_3$ Preparation by Reaction of TiO_2 with $Ba(OH)_2$

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Abstract

The reaction of $Ba(OH)_2$ solution with TiO_2 leads, depending on the conditions, to $TiO_2/BaTiO_3$ mixtures or to $BaTiO_3$. Under relatively mild conditions the reaction leading to $BaTiO_3$ is nearly complete when using anatase, whereas with rutile the reaction occurs only to a small extent. Only reactions with highly dispersed anatase lead to complete $BaTiO_3$ formation. An analogous situation can be found for hydrothermal experiments. The study of the sintering behaviour shows that $BaTiO_3$ powders obtained by reaction of $Ba(OH)_2$ solution with highly reactive anatase can be densified effectively at temperatures ≥ 1200°C.

Die Umsetzung von $Ba(OH)_2$-Lösungen mit TiO_2 führt je nach Reaktionsbedingungen zu $TiO_2/BaTiO_3$-Gemischen bzw. zu $BaTiO_3$. Bei relativ milden Bedingungen kommt es bei Verwendung von Anatas zu weitgehenden Umsetzungen zu $BaTiO_3$, während die Reaktion mit Rutil nur in geringem Umfang abläuft. Zu vollständiger $BaTiO_3$-Bildung führen nur Reaktionen mit hochdispersem Anatas. Die analoge Situation liegt bei hydrothermalen Experimenten vor. Das Studium des Sinterverhaltens zeigt, daß sich die durch Umsetzung von $Ba(OH)_2$-Lösung mit hochreaktivem Anatas entstandenen $BaTiO_3$-Pulver bei Temperaturen ≥ 1200°C effektiv verdichten lassen.

Lorsque l'on fait réagir des solutions de $Ba(OH)_2$ avec du TiO_2, on obtient, selon les conditions mises en œuvre, des mélanges $TiO_2/BaTiO_3$ ou du $BaTiO_3$. Dans des conditions opératoires relativement douces, la réaction conduisant à la formation de $BaTiO_3$ est presque complète lors de l'utilisation d'anatase tandis que la réaction avec le rutile est limitée. La formation complète de $BaTiO_3$ ne se produit que dans le cas de réactions avec de l'anatase hautement dispersé. Une situation analogue peut être trouvé pour des expériences hydrothermiques. L'étude du comportement en frittage montre que les poudres de $BaTiO_3$ élaborées par réaction d'une solution de $Ba(OH)_2$ avec de l'anatase fortement réactif peuvent être densifiées de manière efficace à des températures ≥ 1200°C.

1 Introduction

$BaTiO_3$ has been extensively studied, because it is a material with very interesting dielectric properties. High-purity, stoichiometric titanate powders with small grain sizes are of interest for the preparation of dense multilayer dielectrics, semiconducting ceramics, electro-optic and piezoelectric elements. The preparation of $BaTiO_3$ powders normally takes place by the solid-state reaction at temperatures higher than 1200°C starting from $BaCO_3$ or other Ba salts and TiO_2.[1] The synthesis of $BaTiO_3$ by the reaction of $Ba(OH)_2$ with TiO_2 in aqueous solution has also been reported.[2–6] Hertl[6] described the kinetics of $BaTiO_3$ formation using a mathematical model of the reaction systems which takes into account the distribution of particle sizes of the reactant TiO_2. Another method consists in the synthesis of suitable precursors, from which the titanates are formed as very fine powders with high sintering activity as a result of a thermal decomposition at relatively low temperatures.[7–11] The direct separation of $BaTiO_3$ from the solution is possible likewise by using Ti alkoxides and $Ba(OH)_2$.[12] The titanate powders obtained by wet chemical methods are frequently of submicron particle size and high chemical purity, but they are often strongly agglomerated.

On the other hand, the hydrothermal synthesis yields perovskites of low agglomeration. Some work has been done, to study the evaluation of size, shape and microstrains of $BaTiO_3$ crystallites produced by

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hydrothermal crystallization at 90–180°C and 0·1–1·2 MPa, from amorphous $TiO_2 . xH_2O$ ($3 < x < 8$) gel and aqueous $Ba(OH)_2$.[13]

It is the aim of this paper to investigate the formation of $BaTiO_3$ starting from TiO_2 suspensions in $Ba(OH)_2$ solution. For this reason, different TiO_2 types are tested and the reaction conditions are varied from temperatures of 60 to 90°C at normal pressure up to hydrothermal conditions (250°C, 3·5 MPa). The sintering behaviour of the $BaTiO_3$ powders formed is studied in comparison with that of $BaTiO_3$ samples synthesized by other methods.

2 Experimental procedure

Three different types of TiO_2 were used for the experiments: TiO_2 R1053 (Kronos Titan, Leverkusen, FRG)—100% rutile, TiO_2 M808 (Merck, Darmstadt, FRG)—100% anatase, and TiO_2 B—100% anatase. TiO_2 B was prepared starting from $TiCl_4$ which was added to a 0·1 molar sulphuric acid solution. Aqueous ammonia (13 M) was dropped slowly at 60°C into the clear solution up to pH 7. The suspension was stirred for 1 h, filtered and washed until chloride was not detectable. The precipitate was dried for 12 h at 110°C and then calcined for 3 h at 550°C. The mass loss during calcination up to 1000°C was measured to be 2·5%. The values for the specific surface area of the TiO_2 powders were 4 m^2/g for R1053, 9 m^2/g for M808 and 72 m^2/g for B.

In the first experiments (series 1) 0·2 mol TiO_2 was added to 500 ml of an aqueous solution containing 0·25 mol $Ba(OH)_2$. The suspension was stirred in an argon atmosphere for 8, 16 or 24 h at 60, 70, 80 or 90°C. The suspension was filtered and the solid phase was washed with water and dried at 100°C.

The hydrothermal experiments of series 2 were carried out in closed silica ampoules which were placed in a steel autoclave filled to 50% with water adequate for a filling grade of 0·5. The $Ba(OH)_2$ solutions and amounts of TiO_2, in the concentrations used in Series 1, were added to the ampoules, using the same filling grade of 0·5 as used in the autoclave. The conditions for the experiments were 6, 18 or 36 h at 3·5 MPa and 250°C.

X-Ray diffraction measurements were carried out to study the present phases. From chemical analysis of Ba and Ti, exact assertions as to the chemical composition of the products were possible.

Studies of the sintering behaviour of $BaTiO_3$ obtained by selected experiments of the two series in comparison with that of $BaTiO_3$ powders prepared by other methods were carried out under isothermal conditions at 900, 1200 and 1400°C in air. The powders were compacted (125 MPa) at room temperature without granulometric pretreatment. The shrinkage of the disks was measured after heating step by step utilizing an external micrometer.

3 Results

Table 1 contains the conditions and the results for the experiments of series 1 and Table 2 for series 2. The results obtained by X-ray diffraction measurements and chemical analysis are shown likewise in Fig. 1 and Table 3 for selected examples. Pure $BaTiO_3$ is obtained only in two cases, namely, when TiO_2 B is used and the conditions are high temperature and long reaction time. Experiments with rutile are practically unsuccessful. The formation of $BaTiO_3$ starting from anatase and $Ba(OH)_2$ solution takes place significantly better when TiO_2 B with its high specific surface area is used. Experi-

Table 1. Experimental conditions for series 1 including the resulting phases (from X-ray measurements)[a]

Reaction time (h)	*Temperature (°C)*	*$Ba(OH)_2$ + R1053*	*$Ba(OH)_2$ + M808*	*$Ba(OH)_2$ + B*
8	60	Rutile	Anatase	Anatase
	70	Rutile	Anatase	Anatase
	80	Rutile	Anatase	Anatase/$BaTiO_3$
	90	Rutile	Anatase	Anatase/$BaTiO_3$ (1)
16	60	Rutile	Anatase	Anatase
	70	Rutile	Anatase	Anatase
	80	Rutile	Anatase	Anatase/$BaTiO_3$
	90	Rutile	Anatase/$BaTiO_3$	Anatase/$BaTiO_3$ (2)
24	60	Rutile	Anatase	Anatase (3)
	70	Rutile	Anatase	Anatase/$BaTiO_3$ (4)
	80	Rutile	Anatase/$BaTiO_3$	Anatase/$BaTiO_3$ (5)
	90	Rutile/$BaTiO_3$ (7)	Anatase/$BaTiO_3$ (8)	$BaTiO_3$ (6)

[a] Numbers in parentheses refer to the samples analysed (see Table 3).

Table 2. Experimental conditions for series 2 (250°C, 3·5 MPa) including the resulting phases (from X-ray measurements)[a]

Reaction time (h)	*$Ba(OH)_2$ + R1053*	*$Ba(OH)_2$ + M808*	*$Ba(OH)_2$ + B*
8	Rutile	Anatase	Anatase/$BaTiO_3$
16	Rutile	Anatase	Anatase/$BaTiO_3$
24	Rutile (9)	Anatase/$BaTiO_3$ (10)	$BaTiO_3$ (11)

[a] Numbers in parentheses refer to the samples analysed (see Table 3).

ments under hydrothermal conditions do not lead to a higher yield of $BaTiO_3$ in the products.

A phase transformation of anatase to rutile can be observed in no case from the diffractograms. Table 4 shows the results of analytical and granulometric measurements for $BaTiO_3$ B1 (from series 1, experiment (6)) and B2 (from series 2, experiment (11)) in comparison with the values for a conventionally prepared $BaTiO_3$ C (from $BaCO_3$ and rutile at 1300°C) and for $BaTiO_3$ A obtained directly from the solution by hydrolysis of $Ti(OC_4H_9)_4$ in the presence of $Ba(OH)_2$ (calcined 1 h at 200°C).[11] The powders B1 and B2 show specific surface areas and grain sizes with values between those of A and C. Their impurity content is significantly lower, and the obtained green densities ρ_o after compacting reach values of around 50% of the theoretical density ρ_{th} (6·08 g/cm³).

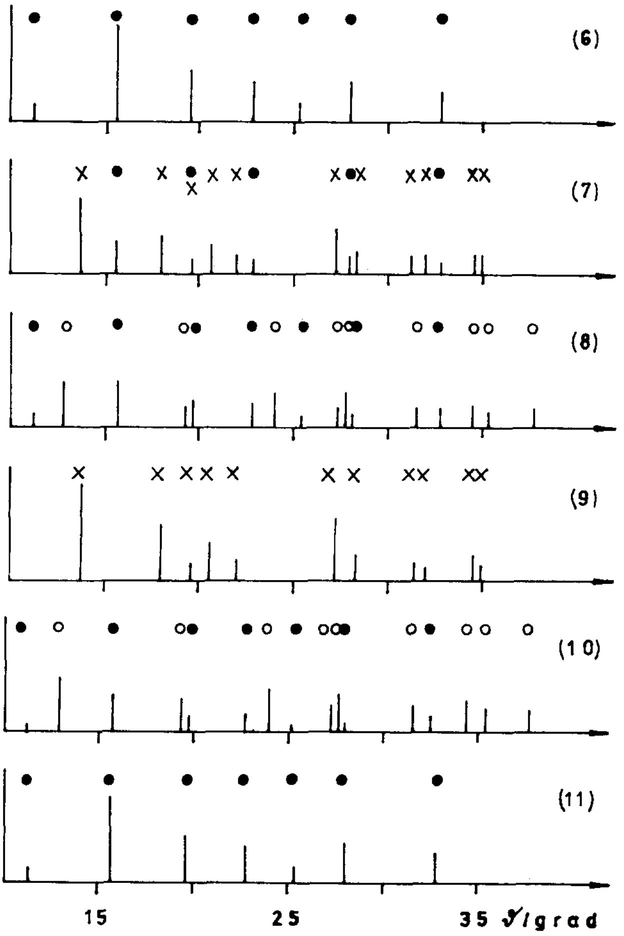

Fig. 1. X-Ray diffraction diagrams of the reaction products of the experiments 6–11: ●, $BaTiO_3$; ○, anatase; ×, rutile.

Table 3. Analytical data of selected experiments (Ba analysis as $BaSO_4$, Ti analysis as TiO_2 after precipitation with cupferron)

Sample	*Ratio of Ba:Ti*	*Composition of the product (% $BaTiO_3$:% TiO_2)*
1	1·0:2·0	50:50
2	1·0:1·3	77:23
3		0:100
4	1·0:5·5	18:82
5	1·0:2·3	43:57
6	1·0:1·0	100:0
7	1·0:6·7	15:85
8	1·0:2·4	42:58
9	1·0:33·2	3:97
10	1·0:4·0	25:75
11	1·0:1·0	100:0

The results of sintering experiments at 1200°C and 1400°C are shown in Figs 2 and 3. The different green densities of the compacts are levelled by using the densification parameter $\alpha = \rho_t - \rho_o/\rho_{th} - \rho_o$ (ρ_t = density dependent on time). At 900°C, only a very small increase of density can be observed. A strong densification during sintering occurs at 1200 and 1400°C growing in the sequence of $BaTiO_3$ C < B2 < B1 < A. The highest density reached for B1 is 5·60 g/cm³ and for B2 5·53 g/cm³ (1400°C, 4 h). The sintering activity of $BaTiO_3$ A is significantly higher than that of B1 and B2.

4 Discussion

The reaction of aqueous $Ba(OH)_2$ solutions with titania to form $BaTiO_3$ is strongly dependent on the

Table 4. Properties of the $BaTiO_3$ powders used for the sintering experiments

	$BaTiO_3$ B1	*$BaTiO_3$ B2*	*$BaTiO_3$ A*	*$BaTiO_3$ C*
Specific surface area (m²/g)	26	12	44	4
d_{BET} (μm)	0·04	0·08	0·02	0·26
Impurities (ppm)				
Al	30	40	120	200
Si	20	30	60	60
Fe	—	—	10	200
Mn	—	—	—	30
Mg	10	20	60	100
ρ_o for compacted powders (g/cm³)	3·03	3·21	2·50	3·71
ρ_{240} (900°C) (g/cm³)	3·08	3·23	2·85	3·71
ρ_{240} (1 200°C) (g/cm³)	4·85	4·83	5·00	4·89
ρ_{240} (1 400°C) (g/cm³)	5·60	5·53	5·80	5·47

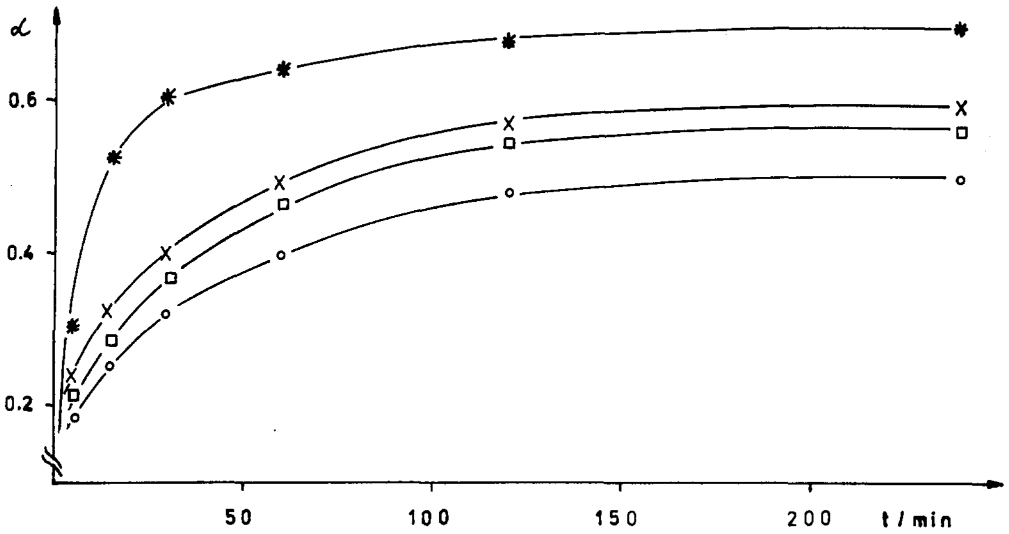

Fig. 2. Densification parameter α of $BaTiO_3$ samples as a function of isothermal heating time at 1200°C: ✱, $BaTiO_3$ A; ×, $BaTiO_3$ B1; □, $BaTiO_3$ B2; ○, $BaTiO_3$ C.

crystallographic and the morphologic properties of the TiO_2. Using rutile with comparatively low specific surface area, only at relatively high temperatures of around 90°C and long reaction times are small amounts of $BaTiO_3$ obtained. The conditions applied for the hydrothermal method do not lead to better results. Anatase powders show in principle a better reactivity in $Ba(OH)_2$ solution. This is explicable from the thermodynamic point of view. The rate of $BaTiO_3$ formation is significantly higher in the case of anatase B with the essentially larger specific surface area. Only by using this TiO_2 type can a complete reaction to $BaTiO_3$ be attained in 24 h. The $BaTiO_3$ formation occurs at first on the surface of the TiO_2 particles. A $BaTiO_3$ product layer is formed and Ba diffusion takes place through this layer to the TiO_2 grains.[6] A large specific surface area connected with small grains and the more reactive anatase form of TiO_2 are therefore favourable for a high reaction rate. The same situation can be registered for the hydrothermal method. The higher temperature as well as the higher pressure lead to a better grain growth connected with the smaller specific surface area and the larger particles for $BaTiO_3$ B2.

The sintering behaviour of the investigated $BaTiO_3$ types is dependent at first on morphologic parameters. The densification rate increases with decreasing grain diameters. The powders with the relatively small particles, a narrow grain size

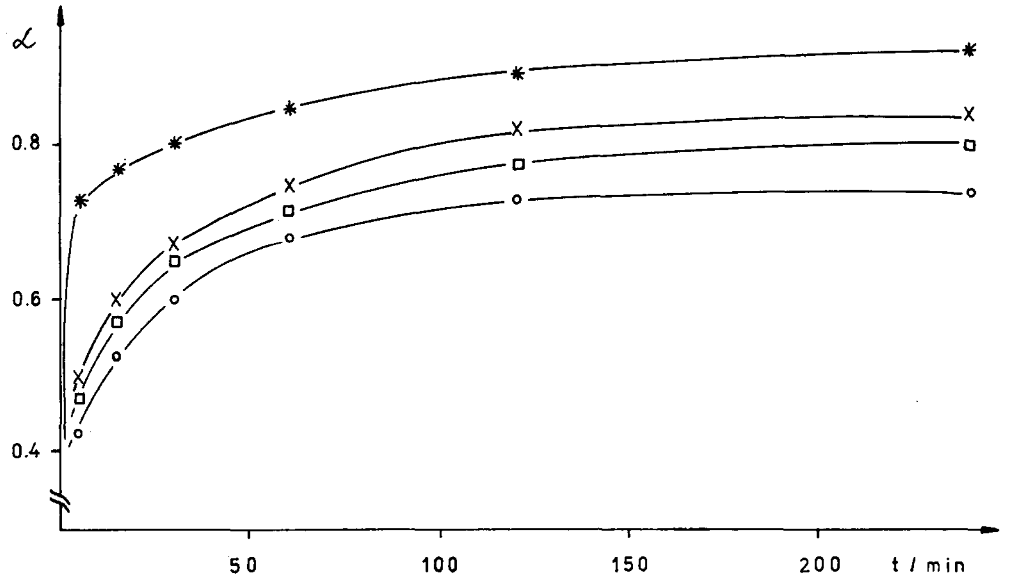

Fig. 3. Densification parameter α of $BaTiO_3$ samples as a function of isothermal heating time at 1400°C: ✱, $BaTiO_3$ A; ×, $BaTiO_3$ B1; □, $BaTiO_3$ B2; ○, $BaTiO_3$ C.

distribution and similar shapes lead to disks with small pores after compacting. The first sintering stage in which the contacts are formed and the necks are rounded is a very rapid one for these samples, and a strong shrinkage is observed, in particular above 1200°C. Deagglomeration of powder $BaTiO_3$ C before compacting and sintering leads likewise to an improved sinterability, which has been described recently.[11] Other studies with $BaTiO_3$ compacts prepared from differently agglomerated powders have shown that the higher the degree of agglomeration, the higher is the sintering temperature to achieve high sintered densities of about 99% of ρ_{th}.[14]

The influence of impurities on the sintering behaviour of $BaTiO_3$ has already been shown.[11] The densification-promoting effect of liquid phases formed by impurities can compensate the disadvantages of $BaTiO_3$ C which result from the unfavourable granulometric situation.

5 Conclusions

The reaction of TiO_2 with $Ba(OH)_2$ solutions to give $BaTiO_3$ under relatively mild conditions as well as under hydrothermal conditions is most successful by using very fine, highly reactive anatase powders. The $BaTiO_3$ powders thus obtained show a high purity and an effective sintering behaviour leading to densities of around 90% of the theoretical value.

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