

Hydrothermal Preparation of Barium Titanate by Transport Reactions

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The hydrothermal synthesis of barium titanate, BaTiO_3 , from barium hydroxide and titanium containing compounds such as titanium esters and freshly precipitated titanium oxide gel was investigated at temperatures from 350°C to 490°C and pressures from 160 atm to 1300 atm. Hydrothermal crystal growth of barium titanate by transport reactions was investigated at temperatures from 460°C to 660°C and pressures from 1120 atm to 3150 atm with a hydrothermal solvent containing sodium hydroxide or potassium fluoride.

Barium titanate crystals were obtained from a 4 M sodium hydroxide solution at 600°C and 2920 atm. Best crystals were prisms of dimensions $0.4 \times 0.4 \times 1$ mm³.

Barium titanate, BaTiO_3 , is one of the most extensively investigated ferroelectric materials. A considerable amount of work has been done on the problem of growing large single crystals of barium titanate. At present growth from binary or ternary melts at temperatures from 1000°C to 1200°C is the most satisfactory method. However, it is desirable to grow single domain barium titanate crystals at lower temperatures. The use of hydrothermal methods is a possibility here. Two alternatives for the hydrothermal preparation of barium titanate single crystals are either synthesis from barium and titanium containing substances or recrystallisation of polycrystalline barium titanate.

Barium titanate can be obtained as a very fine powder by hydrolysis of a titanium ester with a solution of barium hydroxide. Flaschen¹ obtained a product with 1–5 μ particles using this method. Kubo, Kato and Fujita² reported that barium titanate with grain size under 0.1 μ can be obtained by refluxing a titanium oxide gel with a barium hydroxide solution. A preliminary hydrothermal investigation by Christensen and Rasmussen³ and by Christensen⁴ shows that barium titanate can be obtained from barium hydroxide solutions and titanium oxide (anatase), titanium oxide gels, or titanium esters, respectively, when temperatures from 380°C to 500°C and pressures from 300 atm to 500 atm are applied.

The hydrothermal synthesis of barium titanate and hydrothermal crystal growth of the compound have been further investigated.

EXPERIMENTAL

Some characteristic experimental conditions and results are summarised in Tables 1 and 2. The pressure was measured using pressure gauges of the Bourdon type, except for the pressure bomb A, where the pressure was calculated from the temperature and the degree of filling, using the pressure-volume-temperature relations for water.⁵ Fig. 1 is a longitudinal slice of one of the pressure bombs D. The temperatures reported in Table 2 are measured in the thermocouple well at I. The temperatures in the pressure vessel have been measured in air at the positions II, III, and IV (see Fig. 1) with the pressure vessel placed in the furnace. Fig. 2 is a plot of these temperatures *versus* the temperature at I.

All crystalline products were examined with a petrographic microscope, and X-ray powder patterns have been obtained of all products using a Guinier de Wolff camera with $\text{CuK}\alpha_1$ -radiation ($\lambda=1.54051 \text{ \AA}$). In the cases where the unit cell parameters were determined from the Guinier powder patterns by a least squares method (Schousboe-Jensen),⁶ germanium, $a_{\text{Ge}}=5.6576 \text{ \AA}$, was used as an internal standard.

Table 1. Experimental conditions for hydrothermal preparation of barium titanate.

Expt. No.	Composition of charge in mole per cent				Pressure bomb	Temp. °C	Pressure atm.	Time h	Product	Largest crystal dimension mm
1	TiO ₂ (anatase)	BH	H ₂ O		A	420	500	106	BaTiO ₃	0.01
	1.2	2.4	96.3							
2	TiO ₂	BH	NaOH	H ₂ O	A	350	160	70	BaTiO ₃	
	0.5	0.5	3.4	95.6						
3	TiO ₂	BH	NaOH	H ₂ O	B	472	540	97	BaTiO ₃	0.05
	0.5	0.5	1.7	97.3						
4	Ti-ester	BH	H ₂ O		B	490	660	101	BaTiO ₃	
	0.45	0.45	99.1							
5	Ti-ester	BH	NaOH	H ₂ O	B	400	750	60	BaCO ₃	
	0.6	2.2	2.2	95.0					BaTiO ₃	
6	Ti-ester	BH	NaOH	H ₂ O	B	485	700	125	BaTiO ₃	0.04
	1.1	1.1	1.9	95.9						
7	TiO ₂	BH	NaOH	H ₂ O	C	435	1300	96	BaTiO ₃	0.01
	0.75	0.75	3.4	95.1						
8	TiO ₂	BH	NaOH	H ₂ O	C	485	1100	96	BaTiO ₃	0.04
	0.9	0.9	4.0	94.2					BaCO ₃	
9	TiO ₂	BH	KF	H ₂ O	C	410	600	96	BaTiO ₃	0.01
	0.9	0.9	4.0	94.2					BaF ₂	
10	TiO ₂	BH	KF	H ₂ O	C	460	825	96	BaTiO ₃	0.12
	0.9	0.9	4.0	94.2					BaF ₂	

BH: Ba(OH)₂·8H₂O

TiO₂: Titanium oxide gel prepared by hydrolysis of Ti(OC₂H₅)₄ with 1 M HCl.

A: 20 ml pressure bomb, lined with pure silver. Dimensions inside: length 80 mm, diameter 14.7 mm.

B: 99 ml pressure bomb, lined with pure silver. Dimensions inside: length 304 mm, diameter 20.4 mm.

C: 220 ml pressure bomb, lined with pure silver. Dimensions inside: length 415 mm, diameter 26 mm.

The temperature was measured using iron-constantan thermocouples.

There was no temperature difference between top and bottom of the pressure vessels.

Table 2. Hydrothermal recrystallisation of barium titanate by transport reactions.

Expt. No.	Composition of charge in mg		Pressure bomb	Temp. °C	Pressure atm.	Time h	Product	Largest crystal dimension mm
11	BaTiO ₃ 38	15 M NaOH 50	D	660	1120	92	BaTiO ₃	0.1
12	BaTiO ₃ 73	15 M NaOH 270	D	460	1430	65	BaTiO ₃	0.1
13	BaTiO ₃ 500	4 M NaOH 1000	D	605	3150	114	BaTiO ₃	0.25
14	BaTiO ₃ 789	4 M NaOH 1200	D	600	2920	500	BaTiO ₃	1
15	BaTiO ₃ 1260	4 M NaOH 1200	D	620	3030	500	BaTiO ₃	1
16	BaTiO ₃ 1000	4 M LiOH 1100	D	625	1200	168	BaTiO ₃	0.01
17	BaTiO ₃ 1000	4 M KOH 1225	D	625	2040	168	BaTiO ₃	0.25
18	BaTiO ₃ 1000	4 M LiF 1100	D	605	1150	168	no transport of BaTiO ₃	
19	BaTiO ₃ 1000	4 M NaF 1170	D	625	2720	168	BaTiO ₃ BaF ₂	0.5 0.5
20	BaTiO ₃ 1292	2 M KF 1200	D	590	2800	500	BaTiO ₃	1
21	BaTiO ₃ 1072	2 M KF 1200	D	620	3060	500	BaTiO ₃	1

D: 6 ml pressure bomb, lined with pure gold. Dimensions inside: length 190 mm, diameter 6.25 mm. The temperature was measured using chromel-alumel thermocouples.

Hydrothermal synthesis of BaTiO₃

Expts. Nos. 1–3. Crystalline titanium oxide reacts with barium hydroxide to form BaTiO₃ (1), but with a barium chloride solution no reaction to BaTiO₃ is obtained under the same experimental conditions. In the hydrothermal synthesis of barium titanate the solution should be alkaline. In order to improve the crystal formation, freshly precipitated titanium oxide gel was used in the charge and the hydrothermal solution contained sodium hydroxide as well as barium hydroxide. The powder pattern of the product from (2) was diffuse but the product from (3), where the reaction temperature was higher than in (2), gave a sharp powder pattern and small crystals could be observed in the product.

Expts. Nos. 4–6. Titanium esters were used in the charge. In (4) and (6) the ester was Ti(OC₂H₅)₄, in (5) the ester was Ti(OCH₂CH(CH₃)₂)₄. The powder pattern of the product from (4) was diffuse, but the powder pattern of (6), where the hydrothermal solvent contained sodium hydroxide, was very sharp. Apparently it is important that the reaction temperature is over 400–500°C and that the mole percent of sodium hydroxide is at least twice as much as that of the titanium compound. The main part of the product from (5) was barium carbonate, BaCO₃. The alcohol part of the ester was oxidised to form carbon dioxide. (When a solution of 3.1 g freshly recrystallised barium

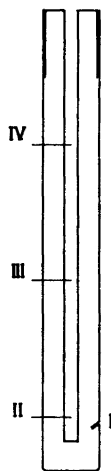


Fig. 1. Longitudinal slice of pressure vessel D. Inside diameter is 6.25 mm, inside length is 190 mm. When the pressure vessel is used the temperature is measured in the thermocouple well at I. A gold ampoule with the charge is inserted in the vessel. II is the position of the nutrients and III is the position of the crystals formed in the hydrothermal recrystallisation.

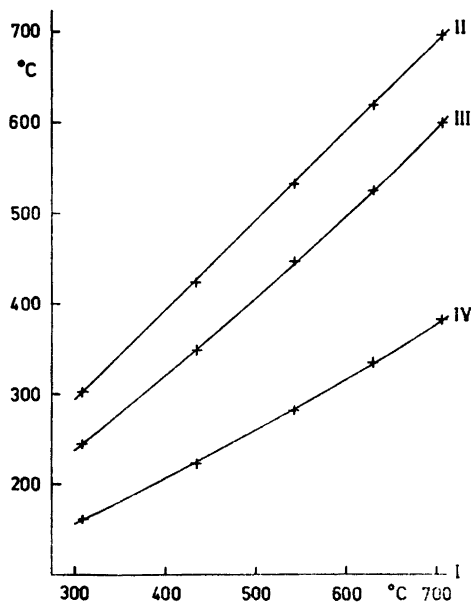


Fig. 2. Plot of the temperatures at positions II, III, and IV (see Fig. 1) measured in air *versus* the temperature at position I, (the thermocouple well). In the temperature range from 300°C to 700°C the temperature difference between I and II does not exceed 10°C.

hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, in 40 ml of carbon dioxide free water was treated with 3 ml of ethanol for 72 h at 425°C and at a pressure of 655 atm, barium carbonate crystals were formed).

Expts. Nos. 7–8. The products from (7) and (8) gave sharp powder patterns. The unit cell parameters of barium titanate obtained from the powder pattern of (8) are $a = 3.994(1) \text{ \AA}$, $c = 4.035(2) \text{ \AA}$ at 25°C.

Expts. Nos. 9–10. Potassium fluoride was used in the solvent instead of sodium hydroxide. This resulted in the formation of barium titanate and barium fluoride, BaF_2 . The product from (9) had a blue colour, and the powder lines of barium titanate were diffuse. A temperature rise (10) improved the crystal size considerably. However, the product was blue in contrast to the usual yellow colour of barium titanate.

Hydrothermal crystal growth of BaTiO_3 by transport reactions

Expts. Nos. 11–12. Barium titanate was prepared by hydrolysis of $\text{Ti}(\text{OCH}_2\text{CH}(\text{CH}_3)_2)_4$ with a solution of barium hydroxide using the preparation procedure described by Flaschen.¹ Single crystals of barium titanate were grown from a melt of 3 g BaTiO_3 ,

and 10.5 g KF, using a modified Remeika technique.⁷ A programmed cooling of the melt of 10°C/h from 1150°C to 1000°C was achieved by pulling the platinum crucible with the melt out of a furnace at a rate of 0.5 cm/h. One single crystal of barium titanate was used in the charges of (11) and of (12). The loss of weight of the crystal was measured as 42 % and 10 %, respectively, corresponding to a transport of 16 mg barium titanate in (11) and 7 mg in (12). Small single crystals of barium titanate were found in the upper cooler part of the gold ampoules. This demonstrates that barium titanate can be transported in a temperature gradient by a hydrothermal solvent containing sodium hydroxide.

Expts. Nos. 13–21. A polycrystalline barium titanate ceramic (Ferropem) was used in the charges. In (14), (15), and (21) all the charge was transported to the upper part of the gold ampoule. The crystals obtained in (13) to (17) were yellow. Many of the crystals were of good optical quality. In (15) were found crystals with largest dimension 0.5–1 mm, where no twinning could be seen in the microscope. However, this product did also contain crystals with domains.

A single crystal from (14) of dimensions $0.1 \times 0.1 \times 0.1$ mm³ was investigated with a precession camera using MoK α -radiation. It was a single crystal with the unit cell parameters $a=3.987$ Å, $c=4.034$ Å at 25°C. The unit cell parameters obtained from the powder pattern of (14) were $a=3.989(1)$ Å, $c=4.032(2)$ Å at 25°C. The unit cell parameters obtained by Rhodes⁸ at 20°C are $a=3.9920$ Å, $c=4.0361$ Å.

The crystals obtained in (19), (20), and (21) were blue. However, the powder patterns were characteristic for barium titanate, and no super structure lines were observed. The unit cell parameters determined from the powder pattern of (21) were $a=3.991(1)$ Å, $c=4.030(1)$ Å at 25°C. Compared with the powder pattern of (14) this is an increase of the a -axes and a decrease of the c -axes. A similar effect was observed in the powder patterns of (19) and (20).

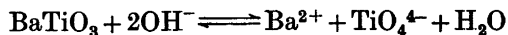
The density of the yellow crystals from (15) and the blue crystals from (21) was determined by the method of Archimedes using carbon tetrachloride for the immersion liquid ($d=1.583$ g/cm³ determined pycnometrically). The values 6.00 g/cm³ and 5.99 g/cm³ were found for the yellow crystals, and for the blue crystals, respectively. The value calculated for barium titanate using the unit cell parameters from the powder pattern of (14) is 6.04 g/cm³. The phase transition near 120°C from tetragonal to cubic structure was investigated on crystals from (15) using the microscope. The transitions were measured three times on three different single crystals and the thermometer used was calibrated using the melting points of acetanilide (114°C) and urea (132.7°C) as standards. The average value of these measurements were 127.6°C for going up in temperature and 126.4°C for going down in temperature, thus giving an average value of 127.0°C for the transformation and a thermal hysteresis of 1.2°C. The transition temperature of the blue crystals from (21) could not be determined using the microscope. Drougard and Young⁹ measured the dielectric constant of barium titanate as a function of the temperature and found that the transition occurred at 122°C going up in temperature and at 120°C going down. Känzig and Maikoff¹⁰ investigated the temperature dependence of the dielectric constant and found that the average value for the transition temperature was 124.53°C with a thermal hysteresis of 1.5°C.

DISCUSSION

Barium titanate is obtained in hydrothermal synthesis from charges containing titanium compounds and barium hydroxide. Products with 0.05 mm crystals were prepared from charges, that also contained sodium hydroxide, the reaction temperature was 470–500°C.

Barium titanate is transported in a hydrothermal solution from higher to lower temperatures in the temperature range from 500°C to 660°C. Yellow single crystals are formed from solutions of lithium hydroxide (16), potassium hydroxide (17), and sodium hydroxide (15). Blue crystals are obtained from solutions of sodium fluoride (19), and potassium fluoride (21). No transport was observed using a 4 M solution of lithium fluoride (18).

With solvents containing the hydroxides of lithium, sodium, and potassium, barium titanate is assumed to be transported as barium ions and titanate ions, and the equilibrium



could possibly be of importance. Crystals obtained from a sodium hydroxide solution are of good quality and single crystals are obtained (15). The transition temperature of barium titanate (15) for the transformation from tetragonal to cubic structure is 127.0°C, significantly higher than the transition temperature of flux grown barium titanate,^{9,10} and the thermal hysteresis is 1.2°C.

The blue crystals of barium titanate obtained from fluoride containing solutions (19) and (21) have powder patterns characteristic for barium titanate. The unit cell parameters of the blue crystals from (19), (20), and (21) are different from those of yellow barium titanate from (14) and (15). The density is 5.99 g/cm³ for the blue compound (21) and 6.00 g/cm³ for the yellow product (15).

Shternberg and Kuznetsov¹¹ investigated the hydrothermal preparation of lead titanate in 10 % potassium fluoride solution. Colourless transparent crystals of lead titanate were prepared from charges with great excess of PbO (PbO—TiO₂ ratio was 5:1 or more), and with a lower ratio in the charge (2:1 to 1:1) where greenish, lead containing titanates formed. These titanates were not further characterised.

Colour centers in barium titanate were investigated by Kosman and Bursian.¹² Two types of coloration, a reddish brownish caused by V-centers and a bluish grey caused by F-centers were reported. The F-centers were formed by keeping barium titanate in a reducing atmosphere at elevated temperatures, and are attributed to oxygen vacancies with trapped electrons.

The blue colour of barium titanate crystals obtained from fluoride containing solutions could possibly be explained by oxygen vacancies, which would cause a change in unit cell parameters and density as well.

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