

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	0.5
20	BaTiO ₃ 1292	2 M KF 1200	D	590	2800	500	BaF ₂	0.5
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

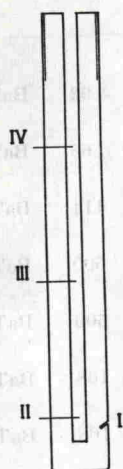


Fig. 1. Longitudinal slice of pressure vessel D. Inside diameter is 6.25 mm, inside length is 190 mm. When the pressure vessel is used the temperature is measured in the thermocouple well at I. A gold ampoule with the charge is inserted in the vessel. II is the position of the nutrients and III is the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

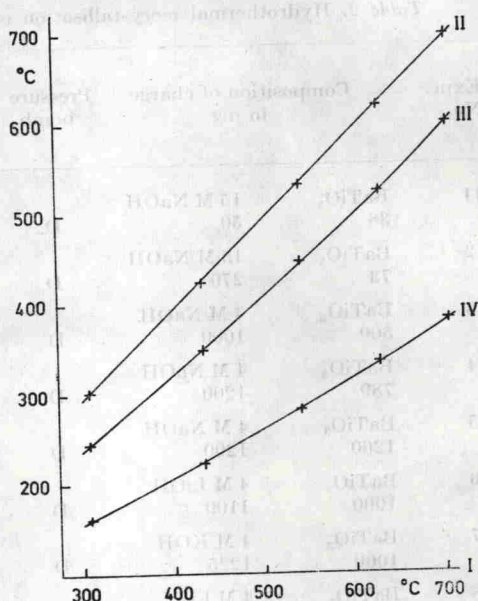


Fig. 2. Plot of the temperatures at positions II, III, and IV (see Fig. 1) measured in air versus the temperature at position I, (the thermocouple well). In the temperature range from 300°C to 700°C the temperature difference between I and II does not exceed 10°C.

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 .