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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 $0.4 \times 0.4 \times 1$ mm^3.

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. Flaschen [1] obtained a product with $1-5$ μ particles using this method. Kubo, Kato and Fujita [2] 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 Rasmussen [3] and by Christensen [4] 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 Cu$K\alpha_1$-radiation ($\lambda = 1.54051$ Å). In the cases where the unit cell parameters were determined from the Guinier powder patterns by a least squares method (Schousboe-Jensen),[6] germanium, $a_{Ge} = 5.6576$ Å, 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) 1.2	BH 2.4		H_2O 96.3	A	420	500	106	$BaTiO_3$	0.01
2	TiO_2 0.5	BH 0.5	NaOH 3.4	H_2O 95.6	A	350	160	70	$BaTiO_3$	
3	TiO_2 0.5	BH 0.5	NaOH 1.7	H_2O 97.3	B	472	540	97	$BaTiO_3$	0.05
4	Ti-ester 0.45	BH 0.45		H_2O 99.1	B	490	660	101	$BaTiO_3$	
5	Ti-ester 0.6	BH 2.2	NaOH 2.2	H_2O 95.0	B	400	750	60	$BaCO_3$ $BaTiO_3$	
6	Ti-ester 1.1	BH 1.1	NaOH 1.9	H_2O 95.9	B	485	700	125	$BaTiO_3$	0.04
7	TiO_2 0.75	BH 0.75	NaOH 3.4	H_2O 95.1	C	435	1300	96	$BaTiO_3$	0.01
8	TiO_2 0.9	BH 0.9	NaOH 4.0	H_2O 94.2	C	485	1100	96	$BaTiO_3$ $BaCO_3$	0.04 10
9	TiO_2 0.9	BH 0.9	KF 4.0	H_2O 94.2	C	410	600	96	$BaTiO_3$ BaF_2	0.01 0.08
10	TiO_2 0.9	BH 0.9	KF 4.0	H_2O 94.2	C	460	825	96	$BaTiO_3$ BaF_2	0.12 0.3

BH: $Ba(OH)_2 8H_2O$

TiO_2: Titanium oxide gel prepared by hydrolysis of $Ti(OC_2H_5)_4$ 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.