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 (Ferroperm) 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 Mo$K\alpha$-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 Rhodes[8] 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 pychnometrically). 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/cm.³ 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 Young[9] 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 Maikoff[10] 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 heigher 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

$$BaTiO_3 + 2OH^- \rightleftharpoons Ba^{2+} + TiO_4^{4-} + H_2O$$
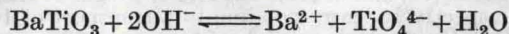
could possibly be of importance. Crystals obtained from a sodium hydroxide solution are of good quality and single crystals are obtained (15). The transition temperature of barium titanate (15) for the transformation from tetragonal to cubic structure is 127.0°C, significantly higher than the transition 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/cm^3 for the blue compound (21) and 6.00 g/cm^3 for the yellow product (15).

Shternberg and Kuznetsov [11] 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 ($PbO - TiO_2$ 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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