The Polymorphic Crystallization of TiO_2 under Hydrothermal Conditions. I. The Effect of Phosphate Ions on the Selective Crystallization of Anatase[1)]

Fujio Izumi and Yoshinori Fujiki
National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31

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The hydrothermal growth of anatase has been investigated at 480—650 °C and 500—1000 atm. Only rutile was formed in KF solutions. On the other hand, anatase was found to crystallize in solutions containing 5 wt% KF+0.1—10 wt% K_2HPO_4 at temperatures up to 600 °C, accompanied by small amounts of $K_2Ti_6O_{13}$ on the addition of 5—10 wt% of K_2HPO_4. The optimum growth conditions were: mineralizer solution, 5 wt% KF+1—2.5 wt% K_2HPO_4; temperature, 550—600 °C; pressure, 1000 atm. Anatase crystals were found as irregular aggregates of dipyramidal grains, blue and transparent. Individual crystals grown at a low supersaturation were characterized by well-developed {101} and {103} faces. The observed habit agrees with the expectations based on Hartman's PBC theory. The presence of phosphate ions favored anatase formation in NH_4F solutions as well, and the retrograde solubility of TiO_2 was observed. The reaction scheme for anatase formation has been proposed. The polymorphic crystallization of TiO_2 under hydrothermal conditions has been shown to be greatly affected by the complexing anions, such as fluoride or phosphate, in mineralizer solutions.

Natural TiO_2 exhibits three structural modifications, the rutile(tetragonal), brookite(orthorhombic), and anatase(tetragonal) minerals. In each of these, the Ti^{4+} ion is surrounded by an irregular octahedron of O^{2-} ions. The number of edges shared by other octahedra increases, from two in rutile to three in brookite and four in anatase, which implies that the free energies of the three forms increase in the above order.[2)] In nature rutile is much more common than brookite and anatase, being formed as a rule at high temperatures. Brookite and anatase transform, exothermally and irreversibly, to rutile over a wide range of temperatures. The rate and activation energy of the anatase–rutile transformation are greatly affected by the concentration of oxygen vacancies or interstitials.[3)] Navrotsky and Kleppa[4)] have demonstrated that anatase is metastable with respect to rutile under all conditions of temperature and pressure.

It is well known that the polymorphic crystallization of TiO_2 from aqueous solutions is influenced by some inorganic anions.[5)] The crystallization of amorphous TiO_2 under hydrothermal conditions leads to brookite in the presence of Na^+ ions.[6,7)] As for natural minerals,[8)] rutile formation is facilitated by the presence of Fe. A lack or deficiency in Fe leads to anatase formation, whereas brookite is preponderantly formed in the presence of Nb.

The only practical method for growing single crystals of rutile in large sizes is that of Verneuil. Other means include solution growth from molten salts,[9—11)] vapor-phase growth by chemical-transport reactions,[9,12)] and the hydrothermal method.[13—16)] Single crystals of brookite can be prepared hydrothermally in NaOH[6)] and NaF[7)] solutions. On the other hand, no authenticated reports have been published on the crystal growth of anatase.

The present study was undertaken in order to establish the optimum conditions for the hydrothermal growth of anatase on a small scale. The hydrothermal method should provide the highest probability of growing large crystals of anatase, since it combines a low temperature and a reasonable solubility. However, it may suffer from the defect that the temperature of the conversion of anatase to rutile is markedly lowered under hydrothermal conditions.[17)] It has now been shown that spectroscopically pure anatase crystals can be successfully grown in KF–K_2HPO_4 solutions. The reaction scheme for anatase formation, as well as some properties and morphology of crystals, has now been investigated.

Experimental

The TiO_2 (rutile) used was obtained commercially and was 99.99% pure. All the other materials used were of a guaranteed reagent grade. The hydrothermal reactions were carried out in sealed Au capsules in cold-seal-type pressure vessels with a capacity of 5.5 cm³ and an inner diameter of 1/4 inch. About 0.1 g of TiO_2 was packed into a nutrient capsule 4 mm in diameter and 15 mm long, with a small hole. This was then placed, together with 0.5 ml of a mineralizer solution, in a larger capsule 5 mm in diameter and 70 mm in length, and sealed by crimping and welding one end shut. This double capsule was placed in the pressure vessel set horizontally with a temperature gradient between the dissolution and crystallization zones. The TiO_2 in the nutrient capsule fixed at one end of the larger one was dissolved, transported by convection to the other end, and recrystallized spontaneously through supersaturation. The nutrient capsule serves as both a container of the starting material and a baffle controlling the growth rate. The reaction temperature was measured by means of a chromel–alumel thermocouple on the outside of the vessel,[18)] while the pressure was measured with a Bourdon gauge. The experiments were conducted at temperatures between 480 and 650 °C and at pressures between 500 and 1000 atm. The temperature difference between the hot and cold zones was 40—90 °C. The duration of the runs was 4—15 days in most cases, but some lasted 25 days.

The reaction products were identified by the X-ray powder diffraction technique. The directions of the crystallographic axes of anatase crystals were found by means of the Wissenberg method. The Miller indices of the crystal faces were determined by use of a reflecting goniometer. The pH values before and after the hydrothermal reactions were measured by Toyo Roshi pH test papers.

Results and Discussion

The experimental conditions and the products of the hydrothermal reactions are summarized in Table 1. In these runs, KF and NH_4F solutions were used with or without additives. Keesmann[6] has suggested that anatase formation under hydrothermal conditions requires both a pH value around neutrality and a temperature below *ca.* 600 °C. The pH values of the 5 wt% solutions of KF and NH_4F were 8.6 and 6.3 respectively, and the hydrothermal solubilities of TiO_2 in these solutions are large enough to effect its crystal growth.[14,15] Therefore, each solution is expected to be advantageous for the hydrothermal growth of anatase.

Effect of Inorganic Ions on the Selective Crystallization of Anatase. The starting material was transported from the hot to the cold zone of the large capsule in KF solutions. Only rutile was formed in 10 wt% KF solutions at 500 °C and 800 atm. Kuznetzov[14,16] also prepared rutile crystals hydrothermally from NaF and KF solutions at 470—585 °C. Judging from the previous finding that, in the presence of F^- ions, rutile crystals grow at the expense of anatase at temperatures as low as 250 °C,[17] anatase would not be formed even if the reaction temperature was lowered to below 500 °C.

It is generally recognized that when TiO_2 is precipitated from an aqueous solution, the presence of a large amount of sulfate or phosphate ions favors anatase formation very strongly.[5] We, therefore, performed hydrothermal reactions in which several materials were added to the KF solution, expecting a similar effect under supercritical conditions (Runs No. 3—No. 7). However, only the addition of K_2HPO_4 proved to be effective in crystallizing anatase. It is worth noting that the presence of Na_2SO_4 did not aid anatase formation; this will be discussed later.

Hydrothermal Reactions in KF–K_2HPO_4 Solutions. Anatase was found to crystallize by adding 0.1—10 wt% of K_2HPO_4 at temperatures up to 600 °C. However, the rate of the transport of TiO_2 fell sharply when only 0.1 wt% of K_2HPO_4 was added. The highest temperature that allows the exclusive formation of anatase lies between 600 and 650 °C because rutile was formed in Runs No. 12 and No. 14. This corresponds well to the temperature of anatase–rutile conversion under hydrothermal conditions.[17]

Small amounts of needle or filamentary crystals, though not more than the minimum detection limit of X-ray powder diffraction analysis, were observed under a microscope in the products formed in solutions containing 5—10 wt% of K_2HPO_4. X-Ray diffraction study showed these crystals to be $K_2Ti_6O_{13}$ elongated along the b axis. The crystallization of the titanate was enhanced by a higher pH value as well as by a higher concentration of K^+. For instance, the addition of 5 wt% of $K_3PO_4 \cdot nH_2O$ (n=2—4) resulted in the formation of only $K_2Ti_6O_{13}$ (Fig. 1). The initial pH of this solution was 12.8. After the hydrothermal reaction, however, the pH was reduced to 6.6. These results can be explained in terms of the following reaction:

$$6TiO_2 + 2K^+ + OH^- \longrightarrow K_2Ti_6O_{13} + H^+$$

As is shown in Table 1, the pH values of KF–K_2HPO_4

Table 1. Transport of TiO_2 in fluoride solutions

Run No.	Mineralizer solution (wt %)	Temperature (°C)	Pressure (atm)	Duration (h)	Change in pH	Products[a)]
1	5% KF	525	875	238		Ru
2	10% KF	500	800	453	8.6→8.4	Ru
3	5% KF+5% $K_2B_4O_7 \cdot 5H_2O$	550	1000	190		Ru
4	5% KF+5% Na_2SO_4	550	1000	168		Ru
5	5% KF+5% K_2WO_4	550	800	261		Ru
6	5% KF+7% $Na_2HAsO_4 \cdot 7H_2O$	550	800	213		Ru
7	5% KF+5% K_2HPO_4	550	1000	185		An
8	5% KF+0.01% K_2HPO_4	550	900	449		Ru
9	5% KF+0.1% K_2HPO_4	550	1000	593		An>Ru
10	5% KF+1% K_2HPO_4	550	1000	263		An
11	5% KF+2.5% K_2HPO_4	600	1000	267	8.6→8.2	An
12	5% KF+2.5% K_2HPO_4	650	1000	305	8.6→6.4	Ru
13	5% KF+5% K_2HPO_4	600	1000	256	8.6→6.6	An$\gg$Ti
14	5% KF+5% K_2HPO_4	650	1000	74		An>Ru $\gg$Ti
15	5% KF+10% K_2HPO_4	550	900	234	8.5→8.6	An$\gg$Ti
16	5% KF+10% K_2HPO_4	600	900	210		An$\gg$Ti
17	5% KF+5% $K_3PO_4 \cdot nH_2O$	600	1000	144	12.8→6.6	Ti
18	$5\%\ KF+\begin{cases}0.5\%\ KH_2PO_4\\4.5\%\ Na_2HPO_4\end{cases}$	560	950	356		An$\gg$Ti
19	$5\%\ KF+\begin{cases}3\%\ KH_2PO_4\\4\%\ K_2HPO_4\end{cases}$	600	1000	474	6.6→6.5	An
20	5% NH_4F	480	500	95	6.3→8.0	Ru
21	5% NH_4F	370	500	89		b)
22	5% NH_4F+2%$(NH_4)_2HPO_4$	480	500	89	6.6→8.8	An>?

a) Ru, rutile; An, anatase; Ti, $K_2Ti_6O_{13}$. b) No transport of TiO_2 occurred.

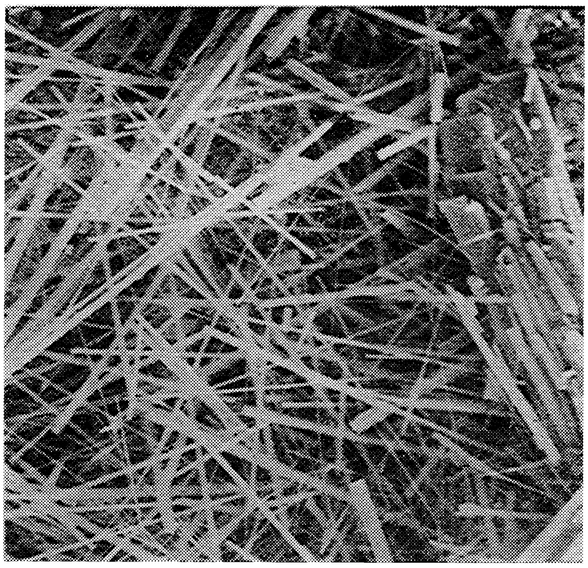

Fig. 1. Needle crystals of $K_2Ti_6O_{13}$.

solutions before and after the hydrothermal reactions did not deviate much from neutrality, since dissolution–crystallization reactions of TiO_2 occurred almost exclusively in these solutions.

In conclusion, the best growth of anatase is achieved under the following conditions: mineralizer solution, 5 wt% KF+1—2.5 wt% K_2HPO_4; temperature, 550—600 °C; pressure, 1000 atm.

Characterization of Anatase Crystals Grown in KF–K_2HPO_4 Solutions. Anatase crystals grown in KF–K_2HPO_4 solutions were usually found as irregular aggregates of dipyramidal grains, blue and transparent (Fig. 2). Upon continued heating at 1000 °C in air, these crystals turned opaque brown.

Individual crystals with maximum dimensions of 1 mm were mostly subhedral, although those grown at a low supersaturation were characterized by well-developed {101} and {103} faces. Hartman's PBC theory(19) predicts the (101) face in anatase to be an F-face and all the other (*h*0*l*) faces to be of the S type. The S-face in the zone [010] with the longest d_{hkl} value is (103). In view of these structural features, the appearance of the {101} and {103} faces on the anatase crystals grown hydrothermally seems to be quite reasonable. The observed habit of the synthetic anatase is in accord with expectations based on the description in the literature(20) that natural anatase occurs in crystals usually showing a simple dipyramid of the second order {101} or, less commonly, {103}.

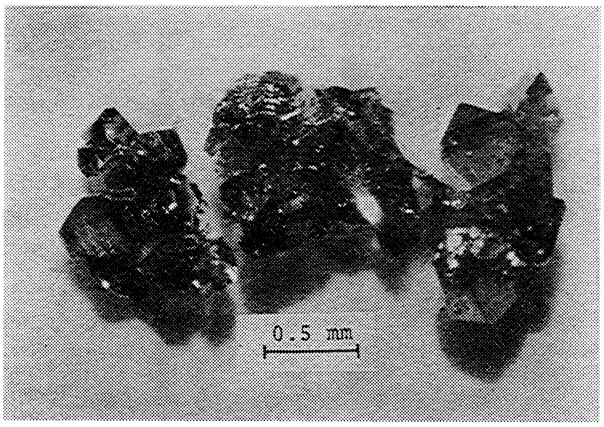

Fig. 2. Aggregates of anatase crystals (Run No. 19).

No impurities could be detected by either the emission spectral analysis or the EPMA analysis of the anatase crystals. The tetragonal unit-cell constants determined by the powder technique are: $a=3.783\pm0.001$ Å; $c=9.508\pm0.002$ Å, which are in good agreement with the data published for anatase. The temperature of the anatase–rutile transformation was measured to be 975 °C by the high-temperature X-ray diffraction method.

Hydrothermal Reactions in NH_4F Solutions. TiO_2 showed retrograde solubility in NH_4F solutions; that is, the transport of the starting material proceeded from the cold to the hot zone of the capsule. From 5 wt% NH_4F solution, only rutile crystallized at 480 °C, and hardly any transport of TiO_2 was observed at 370 °C. On the other hand, anatase was obtained in the presence of 2 wt% of $(NH_4)_2HPO_4$, accompanied by unknown by-products which were found as brownish and translucent solids that formed an aggregate with anatase crystals (Fig. 3) and as a white powder dispersed throughout the whole capsule. The EPMA analysis of the former showed the main constituents to be Ti and P, indicating that it is a kind of titanium phosphate. However, no further effort was devoted to examining this phase in detail. The anatase crystals obtained

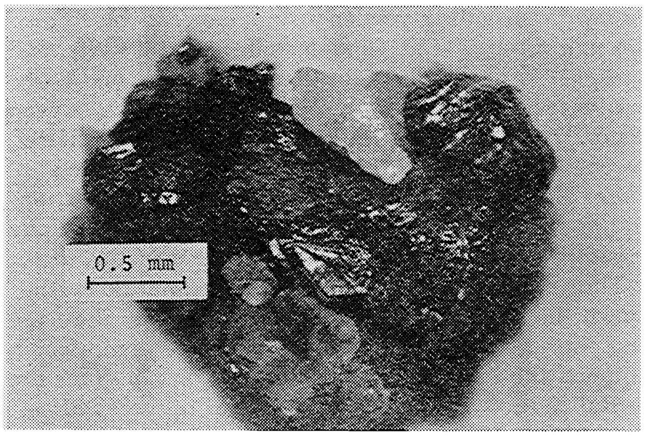

Fig. 3. Anatase crystals accompanied by an unknown phosphate.

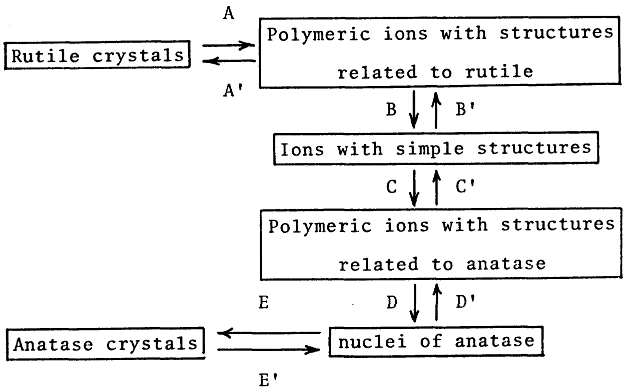

Fig. 4. The reaction scheme for anatase formation under hydrothermal conditions.

were in the form of opaque black grains with an average size of 0.3 mm. These results revealed that the presence of phosphate ions favors anatase formation in NH_4F solutions as well.

The Reaction Scheme for Anatase Formation under Hydrothermal Conditions. The reaction scheme for anatase formation assumed on the basis of the work by Yamaguchi *et al.*[21,22] is illustrated schematically in Fig. 4. The starting material (rutile) reacts with F^-, H_2O, and other species to form polymeric ions with structures related to the lattice of rutile; these ions undergo further cleavage and form ions with simple structures. The resulting ions are unstable under supersaturated conditions; they are hydrolyzed to give polymeric ions with structures related to anatase. Further hydrolysis leads to the formation of the nuclei of anatase, which grow into anatase crystals. Processes A and B should take place in the dissolution zone, whereas Processes C and D are predominant in the crystallization zone.

Caglioti *et al.*[23] have revealed that the $TiOF^+$, $TiOF_2$, $TiOF_3^-$, and $TiOF_4^{2-}$ species exist in aqueous solutions of Ti^{4+} and F^- ions. These mononuclear and/or polynuclear oxyfluoro-complexes are probably formed in the hydrothermal solutions of KF and NH_4F as well, which leads to the selective formation of rutile-like polymeric ions through Process B′. On the other hand, the above species are assumed to be further complexed by phosphate ions in the presence of K_2HPO_4 or $(NH_4)_2HPO_4$, with the result that only polymeric ions with structures related to anatase can be formed through Process C. Complexing between Ti^{4+} and phosphate is quite likely to occur since Ti^{4+}, one of the hardest acids, has a very strong affinity for the oxygen donor.[24] The decrease in the concentration of K_2HPO_4 lowers the rate of Process C, but favors Process B′ (Runs No. 8 and No. 9). Above 600 °C, polymeric ions and/or nuclei with the anatase structure are partially transformed into the denser rutile-type structures.

The emission spectral analysis of the anatase crystals grown in KF–K_2HPO_4 solutions indicates that the phosphorus content does not exceed 10 ppm, which supports the idea that phosphate ions do not enter the crystal lattice of anatase, but are released almost completely into an aqueous environment during Processes C, D, and E. This is understandable in view of the large difference in ionic radius between Ti^{4+} and P^{5+} (Ti^{4+}, 0.69 Å; P^{5+}, 0.25 Å).[25] The failure to crystallize anatase in the presence of Na_2SO_4 may be ascribed to the weaker complexing ability of the sulfate ion compared with that of the phosphate ion.[26]

The detailed mechanism by which the nucleation of anatase occurs in the presence of phosphate ions is still a matter of speculation. However, the data presented in this paper suggest that the polymorphic crystallization of TiO_2 under hydrothermal conditions is greatly affected by the complexing anions, such as fluoride or phosphate, in mineralizer solutions. Work is now under way to investigate this problem in detail.

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References

1) A part of this paper was briefly reported in F. Izumi and Y. Fujiki, *Chem. Lett.*, **1975**, 77.

2) L. Pauling, *J. Amer. Chem. Soc.*, **51**, 1010 (1929).

3) R. D. Shannon and J. A. Pask, *J. Amer. Ceram. Soc.*, **48**, 391 (1965).

4) A. Navrotsky and O. J. Kleppa, *ibid.*, **50**, 626 (1967).

5) "Gmelins Handbuch der Anorganischen Chemie," Titan (1951), pp. 227, 228.

6) I. Keesmann, *Z. Anorg. Allg. Chem.*, **346**, 30 (1966).

7) E. Schwarzmann and K. H. Ognibeni, *Z. Naturforsch.*, B, **29**, 435 (1974).

8) I. Kostov, "Mineralogy," Oliver & Boyd, Edinburgh, (1968), p. 242.

9) I. N. Anikin, I. I. Naumova, and G. V. Rumyantseva, *Kristallografiya*, **10**, 230 (1965).

10) J. S. Berkes, W. B. White, and R. Roy, *J. Appl. Phys.*, **36**, 3276 (1965).

11) T. Sugai and S. Hasegawa, *Yogyo Kyokai Shi*, **77**, 65 (1969).

12) T. Niemyski and W. Piekarczyk, *J. Cryst. Growth*, **1**, 177 (1967).

13) M. L. Harvill and R. Roy, *J. Phys. Chem. Solid*, *Suppl.*, 563 (1967).

14) V. A. Kuznetzov, *J. Cryst. Growth*, **3**, **4**, 405 (1968).

15) M. Passaret, Y. Toudic, A. Regreny, R. Aumont, and J. F. Bayon, *ibid.*, **13**, **14**, 524 (1972).

16) V. A. Kuznetzov, "Crystallization Process under Hydrothermal Conditions," ed. by A. N. Lobachev, Consultants Bureau, New York, N. Y. (1973), pp. 43—55.

17) E. F. Osborn, *J. Amer. Ceram. Soc.*, **36**, 147 (1953).

18) Attention should be called to the fact that the temperatures described in this paper refer to those of the dissolution zones in the case of Runs No. 1—No. 19 and those of the crystallization zones in Runs No. 19—No. 21.

19) P. Hartman, "Crystal Growth: An Introduction," ed. by P. Hartman, North-Holland Publishing Co., Amsterdam (1973), pp. 398—401.

20) C. Palache, H. Berman, and C. Frondel, "Dana's System of Mineralogy," 7th ed., Vol. I, John Wiley & Sons, New York, N. Y. (1963), p. 583.

21) G. Yamaguchi and H. Yanagida, This Bulletin, **36**, 1155 (1963).

22) G. Yamaguchi, H. Yanagida, and T. Fujimaru, *ibid.*, **38**, 54 (1965).

23) V. Caglioti, L. Ciavatta, and A. Liberti, *J. Inorg. Nucl. Chem.*, **15**, 115 (1960).

24) C. F. Bell and K. A. K. Lott, "Modern Approach to Inorganic Chemistry," 2nd ed., Butterworth & Co., London (1966), p. 207.

25) This seems to exclude the possibility for P^{5+} to substitute Ti^{4+} in the anatase structure.[3]

26) For example, when concentrated H_3PO_4 was added to the solution of titanium sulfate, a white precipitate of titanium phosphate was immediately formed.