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HYDROTHERMAL GROWTH OF ANATASE (TiO_2) CRYSTALS

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Anatase crystals were grown hydrothermally using KF-K_2HPO_4 solutions. Only rutile was formed in KF solution, whereas the addition of K_2HPO_4 was effective in crystallizing anatase over a wide range of temperature and pressure. Some properties and the morphological features of the synthetic anatase are described.

Introduction

Natural titanium dioxide exhibits three structural modifications: rutile, brookite and anatase. Each consists of [TiO_6] octahedra sharing two, three and four edges respectively, which suggests that the phase stabilities decrease in the same order. Navrotsky and Kleppa[1)] reported that anatase is metastable with respect to rutile under all conditions of temperature and pressure. The flux, vapor and hydrothermal methods have been used for the purpose of obtaining rutile crystals. On the other hand, no authenticated report has been published on the crystal growth of anatase that is metastable at low-temperature region. In the present work, we established the optimum conditions for the hydrothermal growth of anatase.

Experimental

The hydrothermal reactions were carried out in sealed Au capsules in a Tuttle-type cold-seal vessel, inner diam. 1/4 in.. Titanium dioxide powder was contained in a capsule, inner diam. 4 mm, length 15 mm, with a small hole. This was sealed with 0.5 ml of solvent into a large capsule, outer diam. 5 mm, length 70 mm, by crimping and welding one end shut. This capsule was placed in the hot zone of a pressure vessel set horizontally. The starting material was transferred from the hot to the cold zone of the large capsule. The temperature difference between the two zones was 40-60 °C on the outside of the vessel.

Results and Discussion

Table 1 lists the conditions and products of the crystal growth runs. In these runs, solutions containing 5 wt% of KF were used in common with or without phosfates. Only rutile was crystallized in KF solution at 525 °C and 875 atm. Kuznetzov[2)] also prepared rutile crystals hydrothermally from NaF or KF solution at 470 °C, which suggests that anatase would not be formed even if the reaction temperature was lowered to below 500 °C.

It is generally found that when TiO_2 is precipitated from an aqueous solution, the presence of a large quantity of the sulfate or phosfate ion leads to the selective formation of anatase. We, therefore, performed hydrothermal reactions in the

Table 1. Growth conditions and products

Run	Solvent (wt%)	Temperature (°C)	Pressure (atm)	Duration (hour)	Products*
1	5%KF	525	875	240	Ru
2	5%KF+2.5%K_2HPO_4	600	1000	267	An
3	5%KF+5%K_2HPO_4	525	875	240	An, Ti(trace)
4	5%KF+5%K_2HPO_4	550	1000	185	An
5	5%KF+5%K_2HPO_4	600	1000	285	An
6	5%KF+5%K_2HPO_4	650	1000	172	Ru
7	5%KF+10%K_2HPO_4	550	900	234	An, Ti(trace)
8	5%KF+10%K_2HPO_4	600	900	210	An, Ti(trace)
9	5%KF+5%$K_3PO_4 \cdot nH_2O$	600	1000	144	Ti

* An: anatase, Ru: rutile, Ti: $K_2Ti_6O_{13}$

presence of phosfate, expecting a similar effect under the conditions of far higher temperatures and pressures. The addition of 2.5-10 wt% of K_2HPO_4 was effective in growing anatase at 525-600 °C and 875-1000 atm. The highest temperature that allows the crystallization of anatase seems to lie between 600 and 650 °C, since only rutile was obtained in run 6. The effect of phosfate ion on the crystallization of anatase should be considered.

X-ray diffraction study showed that the needle crystals formed together with anatase at higher concentrations of phosphate were potassium hexatitanate, $K_2Ti_6O_{13}$, elongated along the b-axis. The higher the pH of the solvent and the concentration of K^+, the more the crystallization of $K_2Ti_6O_{13}$ was brought about. For instance, only $K_2Ti_6O_{13}$ was formed on addition of 5 wt% of $K_3PO_4 \cdot nH_2O$. The initial pH of this solution was 12.8, which is far higher than the value 8.6 of 5 wt% KF + 5 wt% K_2HPO_4 solution. After the hydrothermal reaction, however, the pH value was reduced to 6.6. These facts may be explained in terms of the following equation:

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

Anatase crystals grown were usually in an irregular aggregation of obtuse bipyramidal grains, bluish and transparent. Individual crystals with maximum dimensions of 1 mm were characterized by well-developed {101} and {103} faces. Hartman's PBC theory[3] predicts the (101) face in anatase to be a F-face, and all other (h0l) faces to be of the S-type. (103) face has the longest spacing value in the zone [010]. It is, therefore, reasonable that the {101} and {103} faces appeared on the crystals grown hydrothermally at low supersaturation.

The temperature of anatase-rutile transformation was measured to be 975 °C by the high-temperature X-ray diffraction method. The tetragonal unit cell constants determined by the powder technique are: $a_0 = 3.783 \pm 0.001$ Å ; $c_0 = 9.508 \pm 0.002$ Å, which is in good agreement with the published data for anatase.

References

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