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Trachit Change of the $ZrSiO_4$ Single Crystal During Crystal Growth Studied by the $Na_2O \cdot 3V_2O_5$ Flux Method

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The appearance and disappearance of the crystal faces of the $ZrSiO_4$ single crystal during crystal growth under the conditions of a growth temperature of 900 °C and a Δt value (temperature difference) of 1 °C have been studied by means of the $Na_2O \cdot 3V_2O_5$ flux method. A spherical seed prepared from a natural zircon single crystal was used. The c{001}, a{100}, and m{110} appeared at the earliest stage, and next appeared r{115}, u{015}, p{111}, e{011}, and q{021} after 20 h of growth time. However, the u-face, r-face, and q-face disappeared after 400 h, and the c-face and a-face began to disappear after 500 h. The final morphology after 1400 h was a first-order prism and a pyramid consisting of only the m-face and the p-face. It was found that the m-face and the p-face were dominant on a flux-grown $ZrSiO_4$ single crystal, and that this tendency was unchangeable after 2500 h.

$ZrSiO_4$ (zircon) is a widely distributed accessory mineral in ogneous rocks. Ushio et al.[1] have reported the growth of the $ZrSiO_4$ single crystal by means of the $Na_2O \cdot 3V_2O_5$ flux method, using a natural zircon seed, the growth rate with the time; the normal growth rates of the c-face, the a-face, the p-face, and the m-face; the growth patterns on the p-face and the m-face; the step-advanced rates of the growth layers on the p-face and the m-face, etc. In this crystal-growth procedure, when a spherical seed was used, the trachit change in the crystal face was observed according to the increase in the growth time. An attempt to reproduce this interesting phenomenon is elucidated in detail.

The trachit change in a crystal may be caused by the different rates of growth of the various faces. A large number of factors can affect the trachit change of a crystal, e.g., the type of solvent, the pH of the solution, the degree of supersaturation or supercooling, the temperature of the crystal growth, the presence of impurities, the rate of cooling, the degree of agitation, the presence of a surface-active agent (surfactant), the flow of solution, the presence of defects (dislocation, twinning, and so on.), the growth time, and frequency and intensity of applied ultrasonic waves.[2]

In this paper, the purpose is to investigate, in detail, the trachit change in the crystal face of a zircon crystal in the initial, intermediate, and final stages, when the zircon crystals are grown slowly by means of the $Na_2O \cdot 3V_2O_5$ flux method using of natural spherical seeds.

Experimental

The experimental apparatus and the configurations of the crucible were previously reported.[1] The inner volume of the platinum crucible was ca. 400 ml, and natural zircon single crystals from Viet Nam and Brazil were used as seeds. There was no difference between the two crystals except for the number of cracks and their colors. The natural zircon single crystals were cut and their surfaces polished to a spherical form close to a true sphere about 5 mm in diameter.

The starting materials of oxides (V_2O_5, ZrO_2, and SiO_2) and a carbonate (Na_2CO_3), used as flux and nutrient, were used as the first-class reagents.

Runs were carried out under the conditions of 900 and 1000 °C for growth temperature (near the upper part of the nutrient) and 0.5 to 5 °C for Δt, which signifies the temperature difference between the seed and the upper part of the nutrient. The growth temperature, the supersaturation, and, especially, the growth time may have a influence on the trachit change in the crystal surface. For this reason, these factors have been controlled electrically as much as possible.

A 800 g portion of the flux and 120 g of the nutrient were charged into the platinum crucible. After confirming the saturation by the nutrient dissolved into the flux melt, a spherical seed tied up with a platinum wire was inserted into the flux melt. The growing seed was pulled up from the flux melt after having soaked for the fixed growth time, and then washed a hot alkaline solution and acid to dissolve the flux solid adhering to the seed surface. After observing the crystal surface of the growing seed with microscopes, this seed was again soaked in the melt. This procedure of inserting the seed into the flux melt and then pulling it, was repeated 30 times.

To identify the grown crystal faces of the zircon seed, an inclination-angle microscope and a scanning electron microscope were used. The former was used mainly to measure the angle between the two grown crystal faces of zircon seed, but also to confirm the existence and shape of the grown crystal faces.

Results

A run carried out under the conditions of a growth temperature of 900 °C and a temperature difference of 1 °C will now be described.

After 20 h of growth time, c{001} appeared in the neighborhood of poles, and a{100} and m{110} in the equator, but at this early stage, all the faces developed as flats and did not yet come into contact with one another. Small pyramid faces of r{115}, u{015}, e{011}, and then q{021} appeared between the c-face and the m- or a-faces.

After 50 h, pairs of faces, namely, the c-face and the r-face, the c-face and the u-face, the p-face and the w-face, the e-face and the q-face, the w-face and the m-face, and the q-face and the a-face, came into contact with each other, and then, appearance marked each step. At the growth time between 120 and 250 h, two groups of steps consisting of c-u-e-faces and c-r-p-faces were observed. However, the u-face and the r-face, the e-face

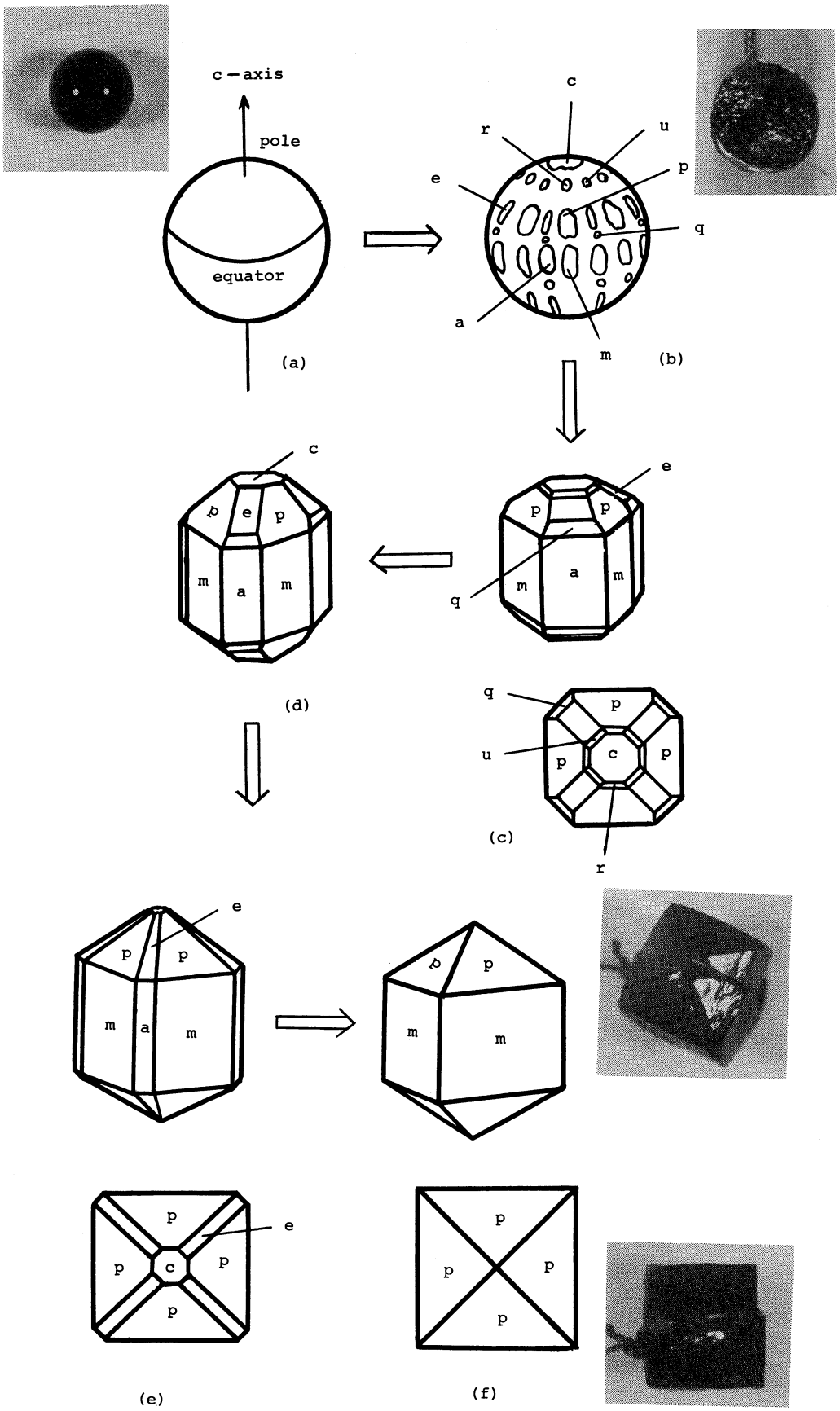

Fig. 1. Schematic drawing of appearance and disappearance of crystal faces during growth.
(a): Spherical seed. (b): after growth time between 20 and 100 h. (c): after 300 to 400 h. (d): 500 to 700 h. (e): after 900 to 1200 h. (f): after above 1400 h.

Table 1. Experimental Results of Interfacial Angle of Grown Zircon Xrystal

Angle between two faces	$Angle_{obsd}$
r{115}∧m{110}	79±0.5°
p{111}∧m{110}	45±0.5°
w{221}∧m{110}	29±0.5°
u{015}∧ a{100}	82±0.5°
e{011}∧ a{100}	57±0.5°
q{201}∧ a{100}	38±0.5°
e{011}∧e'{011}	46±0.5°
p{111}∧p'{111}	57±0.5°

and the p-face, and the m-face and the a-face did not make contact with each other.

After 300 h, the crystal domain of both c-u-e-faces and c-r-p-faces got much bigger, and the lateral faces of the a-face and the m-face came into contact with each other. The u-face, the r-face, the q-face, and the w-face disappeared after 400 h, while the c-face, the e-face, and the p-face grew further.

After 500 h, the p-face and the e-face were observed as pyramid faces, but the crystal-surface domain of the p-face was better developed than that of the e-face. After 700 h, the c-face and the a-face began to disappear. The e-face was also found to disappear.

After 900 h, only the p-face as a pyramid face and m-face as a lateral face grew much larger. The very small c-face, the e-face, and the a-face still remained, but these faces disappeared as growth went on.

The morphology after 1400 h was a first-order prism and a pyramid consisting of only the m-face and the p-face. The grown seed was elongated only in the direction of the *c*-axis after 2000 h and was bounded with the same faces. It was found that the m-face, and the p-face were dominant on the flux-grown $ZrSiO_4$ single crystal, and that this tendency was unchangeable after 2500 h.

A schematic drawing of the trachit changes during the growth of the $ZrSiO_4$ single crystal is shown in Fig. 1, while experimental results of the interfacial-angle measurements given in Table 1.

In the case a growth temperature of 1000°C, each face appeared and disappeared much faster than was the case at 900°C, while in the case of the same growth temperature, e.g., at 900°C, the increasing temperature difference had a tendency to promote the growth rate of each face.

Discussion

As has been mentioned above, the habit and trachit changes of a crystal are influenced by various factors.

The crystal faces most frequently observed in the natural zircon single crystal were c{001} as a basal face, m{110} and a{100} as prisms, and p{111}, u{331}, x{3ll} and e{011} as pyramids.[3]

By using a spherical and natural zircon single crystal as a seed, a basal c-face and prisms of the a-face and the m-face near the equator appeared mainly in the earliest stage, and then c-r-p-m-faces and c-u-q-a-faces appeared between the pole and the equator of a spherical seed. These faces made several flights of steps. Among these faces, the growth rate increase of the u-face, the r-face, and the q-face was much faster, and these faces also disappeared much faster. Judging from the experimental results on the order of disappearance, the u-face and the r-face disappeared almost simultaneously, and after a while the q-face disappeared. Then surface of the c-face became apparantly rough, and finally disappeared. The final crystal form was bounded by the p-face as a pyramid and the m-face as a prism in this experimental range. These faces were a prism and a pyramid of the first order. An a-face, etc., forming a prism and the pyramid faces of the second order disappeared. No w-face formed between the p-face and the m-face was observed because of the very high growth rate. A w-face belongs to the pyramid of the first order. Pyramid faces of the second order, e.g., the e-face, the u-face, and the q-face, remained from 900 to 1200 h.

From a stereographic projection for a crystal of zircon, a continuous series of steps of the c-u-e-q-a-faces would be observed in the direction of the *a*-axis if each face appeared, and we could expect a continuous series of steps of the c-r-p-w-m-faces to appear in the direction inclined at 30°C from the *a*-axis. No x-face was observed because of the higher growth rate.

Hartman[4] reported the morphology of zircon by applying the periodic-bond-chain theory, and calculated the lattice energy and the attachment energies of several faces. He concluded that, if it was assumed that the displacement velocities of the F-faces were proportional to the attachment energies, a "theoretical habit" of zircon crystals was bounded by two forms only: a{100} and e{011}.

These faces produced an "equilibrium form" and were a second-order prism and a pyramid. However, as has been stated previously, the "growth form" of the zircon single crystal prepared in this experiment was bounded by the first-order prism and pyramid faces, i.e, m{110} and p{111}. In comparison with the Kombinationspersistenz (*P*-value) and the Fundortspersistenz (*F*-value),[4,5] it was found that these values of crystal faces producing both forms, e.g., the equlibrium and growth forms, were relatively closer than those of the other faces. For this reason, it may be assumed that the ease of formation of both forms is influenced by the environmental conditions surrounding a zircon crystal, e.g., the kinds of the solute and the solvent and growth temperature.

From Hartman's result from the calculation of the attachment energies of the crystal faces of zircon by using the electrostatic energy, the order of attachment energy was found to be follows:

$$a\{100\} < m\{110\} < e\{011\} < p\{111\} < c\{001\}$$

The attachment energy of a {100} was the smallest one, m{110} ranked second, and so on. The F-face (flat face) is a{100}, m{110}, e{011}, if we considers the P.B.C vector numbers. It is possible that a F-face has a higher attachment energy than a S-face (stepped face) has. The c-face, the u-face, the r-face, the p-face, the m-face, and the a-face were observed in the initial stage of crystal growth, but trachit change was observed with the crystal growth proceeding and only the p-face and m-face were finally observed. In this experimental result, the growth form of zircon single crystal was a tetragonal prism with a bipyramid, bounded by the p-face and the m-face only. From these experimental findings concerning the appearance and disappearance of each face from the observed normal growth rates, the order of the normal growth rate for each face of zircon single crystal was determine to be as follows:

$$a\{100\} > c\{001\} > p\{111\} > m\{110\}$$

The observed value of the normal growth rate of the a-face was $5.0—7.0\times10^{-4}$ mm h^{-1}; the c-face, $2.0—3.5\times10^{-4}$ mm h^{-1}; the p-face, $1.2—2.0\times10^{-4}$ mm h^{-1}, and the m-face, $0.9—1.0\times10^{-4}$ mm h^{-1}.[1] From this fact, when a spherical crystal was used as a seed, the pyramid face appeared mainly in the initial stage, but almost disappeared in the intermediate stage because of the higher growth rates. A c-face as a basal face appeared mainly in the initial stage and remained until the final stage, but soon disappeared. Therefore, a normal growth rate for each face can be presumed to be one in which the trachit of growth in the zircon single crystal changes.

A small zircon single crystal grown by spontaneous nucleation formation at the bottom or on the wall of the crucible was bounded by the m-face and the p-face, which grew progressively greater, and by very small faces, e.g., the a-face, the q-face, and the c-face. At the bottom of the crucible, the growth rate of the zircon single crystal was usually slower in order to have a small temperature difference and a small convection velocity of the flux melt. Therefore, it was expected that a zircon single crystal was grown by a phenomenon close to the diffusion process. Small crystal faces of the a-face, the q-face, the c-face, etc. may remain without disappearing.

A process in which the solute molecule is carried to a seed by heat convection and incorporated in a seed surface may occur, but the process in which the solute is carried by a phenomenon close to heat convection, and therefore a seed grows, may more probably be expected.

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