

SHORT
COMMUNICATIONS

Growth Rate of the {0001} and {01 $\bar{1}$ 1} Faces of Quartz as a Function of Temperature

G. T. Ostapenko and B. M. Mitsyuk

Institute of Magnetism, National Academy of Sciences of Ukraine, pr. Vernadskogo 36b, Kiev, 03680 Ukraine

e-mail: ostap@imag.kiev.ua

Received December 15, 2005

DOI: 10.1134/S0016702906120081

INTRODUCTION

The growth and dissolution rates of quartz in water and various aqueous solutions have long been studied by many researchers. A polar diagram was constructed for the growth rate of main quartz faces and other artificial surfaces [1–3]. However, an important kinetic parameter, the activation energy of the growth of various quartz faces, requires further refinement. In particular, Laudise [4] fairly reliably determined an activation energy of ~20 kcal/mol (or 84 kJ/mol) for the growth rate of the {0001} basal face (growth from 0.5 M NaOH solution at a degree of autoclave filling of 0.8 and a temperature interval of 300–400°C). At the same time, the values of activation energy for minor rhombohedral (~14 kcal/mol) and large rhombohedral (~24 kcal/mol) faces were only approximately estimated [4] on the basis of two experimental points (these values were referred to as test ones by Laudise [4]).

The activation energy of the growth of the basal plane and artificial prisms $+x$ [11 $\bar{2}$ 0] and $-x$ [$\bar{1}$ 120] (growth from 0.5 M NaOH, N₂CO₃ and KOH, K₂CO₃, and KHCO₃ solutions at a degree of autoclave filling of 0.75 and a temperature interval of 330–400°C) were determined by Chernov and Kuznetsov [5]. According to these authors, the logarithm of the growth rate of the basal plane in NaOH and KOH solutions shows nonlinear dependence on reciprocal temperature (similar nonlinearity was observed for faces $+x$ and $-x$). Chernov and Kuznetsov [5] determined the activation energy of growth for the basal plane (19 and 21 kcal/mol for NaOH and KOH solutions, respectively) and $+x$ and $-x$ prisms (26 and 27 kcal/mol, respectively) from the slope of the curve of the logarithm of rate versus reciprocal temperature at a temperature of 370°C. The nonlinear dependence of the logarithm of rate on reciprocal temperature was explained by the effect of adsorption of own particles on crystallization kinetics in more alkaline solutions, as well as by changes in the surface relief [5].

Rumyantsev [6] studied the effect of various cations and anions in aqueous solutions on the dissolution and crystallization kinetics of the {0001}, {01 $\bar{1}$ 1}, and {10 $\bar{1}$ 1} faces of quartz; he also considered other important problems, including the existence of an absorbed water film on the quartz surface, silica polymerization, etc.

EXPERIMENTAL METHODS AND RESULTS

This paper reports an experimental study of the growth rate of the basal {0001} and minor rhombohedral {01 $\bar{1}$ 1} faces. The classical technique of temperature drop (ΔT) was applied [1–4]. Experiments were performed in an autoclave, 350 mm long, 35 mm outer diameter, 17 mm inner diameter, and 70 cm³ internal volume. The autoclave hole was closed from two ends by seals with cylindrical pockets (4 mm diameter, 15 mm long, and 1 mm wall thickness) extending into the dissolution and crystallization zones, where a chromel–alumel thermocouple was inserted. This allowed us to measure temperature in the dissolution and crystallization zones with a relatively high accuracy.

A long quartz plate (120 × 14 × 2.5 mm) oriented along the {0001} plane was placed into the dissolution zone (high temperature), and two smaller (14 × 10 × 2.5 mm) quartz plates oriented along {0001} and {01 $\bar{1}$ 1} were placed into the crystallization zone. The plates were preliminarily etched to remove the disturbed layer. The area of the short plates was six times smaller than the area of the long plate. It is known [1, 4] that in this case the growth rate is independent of the ratio of dissolution to crystallization areas. Under such conditions at 5% opening of the baffle between the dissolution and crystallization zones, the concentration near the surface of the growing {0001} and {01 $\bar{1}$ 1} plates was obviously maintained equal to that in the dissolution zone, which provided supersaturation (ΔC) proportional to the temperature drop ΔT [1, 2, 7]. The identical values of the growth rate of quartz plates

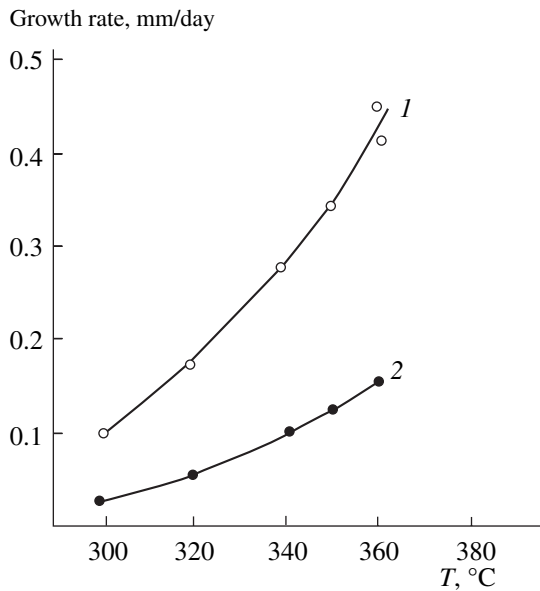


Fig. 1. Temperature dependence of the growth rates of the (1) {0001} and (2) {01 $\bar{1}$ 1} faces of quartz in 1 M NaOH solution at a pressure 1 kbar and a temperature drop of 10°C.

obtained in some runs in the lower (near the baffle) and the upper (near the temperature “pocket”) growth zones confirm that the supersaturation was approximately uniform in this zone. The filled autoclave was heated to given bottom and top temperatures for one hour. The autoclave was filled with an alkaline (1 M NaOH) solution already saturated in silica. Owing to the use of saturated solution, the initial stage of crystal dissolution was practically eliminated and, correspondingly, the growth of {0001} and {01 $\bar{1}$ 1} quartz crystals at the expense of the dissolution of the large quartz plate began immediately after the attainment of experimental conditions.

The growth rates of the {0001} and {01 $\bar{1}$ 1} faces (in a direction normal to them) were determined at temperatures of 300, 320, 340, 350, and 360°C and a temperature drop 10°C. The degree of autoclave filling was 0.8, which provided a pressure of about 1 kbar [8]. The experimental conditions and results are shown in the table and Figs. 1 and 2. The following observations can be made.

(1) The proportions between the growth rates of the {0001} and {01 $\bar{1}$ 1} faces remain approximately constant (about 3), which is somewhat higher than previously reported values [1, 2].

(2) The growth rates (V) of the {0001} and {01 $\bar{1}$ 1} faces increase with temperature following the Arrhenius exponential relation. The almost identical slopes of the curves of the logarithms of growth rates as functions of reciprocal temperature for the two faces (Fig. 2) indicate that the activation energies of growth

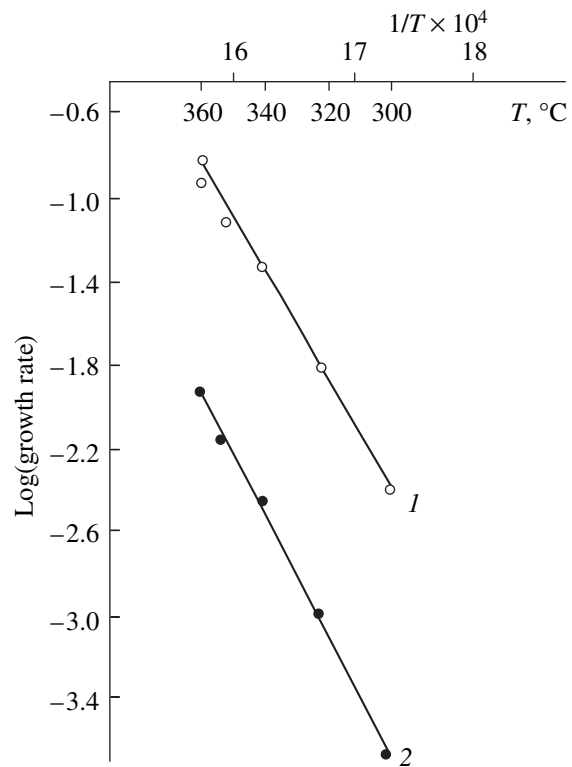


Fig. 2. Linear dependence of the logarithm of the doubled growth rate of the (1) {0001} and (2) {01 $\bar{1}$ 1} faces of quartz on reciprocal temperature ($1/T$) in 1 M NaOH solution at $\Delta T = 10^\circ\text{C}$ and $P = 1$ kbar.

of the {0001} and {01 $\bar{1}$ 1} faces are very similar and close to $20 \pm (1-2)$ kcal/mol [or $84 \pm (4-8)$ kJ/mol]. This result coincides with the aforementioned activation energy estimated by Laudise [4] for the {0001} face. At the same time, an activation energy of 20 kcal/mol obtained by us for the {01 $\bar{1}$ 1} face is different from 14 kcal/mol reported in [4]. It was noted above, that the latter value cannot be considered highly accurate.

Let us briefly consider, following Chernov [7], the growth rates of the basal and minor rhombohedral faces. The basal face of quartz is classified as a rough K-face growing by the normal mechanism at the expense of the incorporation of particles into the kinks on the face surface. The growth rate at the kink of this face is specified by the expression [7]

$$V = \alpha v (\alpha/\lambda_k)^2 \exp(-E/kT) \Omega (C - C_0), \quad (1)$$

where C_0 is the equilibrium concentration of particles in the solution; C is the concentration of particles near the surface and the kink, which approaches the concentration in the solution volume (see below); α is the average size of particles in the crystal; Ω is the volume of a particle in the crystal; λ_k is the distance between kinks ($\lambda_k \approx 3\alpha$); $(\alpha/\lambda_k)^2$ is the probability of the encounter of a

dissolved particle of the crystal with a kink; ν is the vibrational frequency of particles ($\sim 3 \times 10^{12} \text{ s}^{-1}$); E is the activation energy; k is the Boltzmann constant; and T is the absolute temperature. The basal surface has a characteristic cellular structure of the cobbled type [1, 2].

The face of a minor rhombohedron can be classified as a smooth F-face with a layer-by-layer growth mechanism. This type of growth is provided by the tangential displacement of a step echelon with a height corresponding to the size of one (α) or several particles ($n\alpha$). The steps are generated by spirals of conical growth hillocks typical of the faces of small rhombohedra [9]. The growth rate of such a face in a normal direction is given by the expression [7]:

$$V = (\alpha/\lambda)\nu, \quad (2)$$

where α is the step height equal in this case to the particle size; λ is the distance between steps; and ν is the velocity of step movement in a tangential direction. The step can be considered as a band of rough surface with kinks [7]. If the velocity of its movement is controlled by the incorporation of particles into kinks, the expression for ν will be similar to the equation for the normal velocity V of a rough surface (Eq. 1) [7]:

$$\nu = \alpha\nu(\alpha/\lambda_k)\exp(-E/kT)\Omega(C - C_0). \quad (3)$$

The difference is that (α/λ_k) is in the first degree. If the step height (h) equals $n\alpha$, the tangential rate ν will be given by a formula similar to Eq. (1).

The energy states of kinks (i.e., energy of the broken bonds) on the basal surface and on the step of a minor rhombohedral face are approximately similar. Hence, the activation energies for the faces of the basis and minor rhombohedra given by Eqs. (1) and (2) with allowance for Eq. (3) must be approximately equal, which is consistent with experiments.

These considerations are valid under conditions that the crystallization rates on the described faces are controlled by the surface reactions of particle incorporation into kinks, and the diffusion component of crystallization rate related to the transfer of particles across the boundary layer with a thickness of δ is small and similar for both faces. The latter condition is provided by (1) the rapid convective mixing of volume solution [1–3]; (2) high diffusion coefficient of silica particles in the solution (about $10^{-4} \text{ cm}^2/\text{s}$) at very low activation energy of this diffusion (about 2.5–3.0 kcal/mol) [10]; (3) small value of δ , up to a monolayer under hydrothermal conditions [5, 11]. Therefore, the concentration C near the surface of faces is close to volume concentration.

As follows from Eqs. (1)–(3), the growth rates of basal and minor rhombohedral faces are proportional to the kink density on their surfaces [7]. This density is more or equal $(1/\lambda_k)^2$ on the basal face and is lower on the face of minor rhombohedra and is equal to $(1/\lambda_k)(1/\lambda)$ at $h = \alpha$ or $(1/\lambda_k)^2(h/\lambda)$ at $h = n\alpha$, where $\lambda \square \lambda_k$ and $\lambda > h$.

Growth rates of the {0001} and {01 $\bar{1}$ 1} faces of quartz within the temperature range 300–360°C (1M NaOH solution, $\Delta T = 10^\circ\text{C}$, $P = 1 \text{ kbar}$)

Run no.	Temperature, °C	Growth rate, mm/day	
		{0001}	{01 $\bar{1}$ 1}
455a	360	0.44	0.15
477a	360	0.41	–
452a	350	0.34	0.11
452b*	350	0.33	0.12
450	350	0.36	0.13
448a	350	0.31	0.11
442c	340	0.27	0.09
480c	320	0.17	0.05
485a	300	0.09	0.03

* Plates of the {0001} and {01 $\bar{1}$ 1} faces were placed directly near the baffle.

ACKNOWLEDGMENTS

We are grateful to V.E. Khadzhi, F.A. Belimnenko, L.A. Gordienko, I.B. Makhina, and A.A. Mar'in for helpful discussions on the problems of quartz growth and quartz plates for experiments.

REFERENCES

1. R. A. Laudise and R. L. Parker, *The Growth of Single Crystals* (Bell Telephone Lab., Murray Hill, 1970; Mir, Moscow, 1974).
2. V. E. Khadzhi, L. I. Tsinober, L. M. Shterenlikht, et al., *Synthesis of Minerals* (Nedra, Moscow, 1987) [in Russian].
3. *Synthesis of Minerals*, Vol. 1 (VNIISIMS, Aleksandrov, 2000) [in Russian].
4. R. A. Laudise, "Kinetics of Hydrothermal Quartz Crystallization," *J. Am. Chem. Soc.* **81**, 562–566 (1959).
5. A. A. Chernov and V. B. Kuznetsov, "Kinetics of Hydrothermal Crystallization of Quartz in Various Solutions and the Hypothesis of an Absorption Film," *Kristallografiya* **4**, 879 (1969).
6. V. N. Rumyantsev, "Effect of the Mineral-Forming Environment on the Kinetics of Quartz Dissolution and Crystallization in Hydrothermal Conditions," *Zap. Vses. Mineral. O-va* **72**, 136 (1993).
7. A. A. Chernov, E. I. Givargizov, Kh. S. Bagdasarov, et al., *Modern Crystallography*, Vol. 3: *Crystal Growth*, Ed. by B. K. Vainshtein, A. A. Chernov, and L. A. Shuvalov (Nauka, Moscow, 1980; Springer, Berlin, 1984).
8. L. A. Samoilovich, "Correlation between Pressure, Temperature, and Density of Aqueous Salt Solutions," Preprint of VNIISIMS, Moscow, 1969 [in Russian].
9. V. S. Balitskii, *Experimental Study of Rock Crystal Formation* (Nedra, Moscow, 1978) [in Russian].
10. V. N. Balashov, Extended Abstract of Doctoral Dissertation in Geology and Mineralogy (Chernogolovka, 1992).
11. G. F. Ershova, Z. M. Zorin, and N. V. Churaev, "Temperature Dependence of the Thickness of Polymolecular Water Films on the Quartz Surface," *Kolloid. Zh.* **37**, 208 (1975).