Determination of the specific surface free energy of natural quartz crystals using measurement of contact angle of liquid droplets

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Contact angle of water and formamide droplets on natural quartz crystals were observed. The specific surface free energy (SSFE) of m, r, and z faces, calculated using the Fowkes approximation, were approximately 54-69 mN/m. The length of the normal line from the center of the crystal to each face (h_i) was observed and compared with the SSFE. Though, Wulff's relationship was well satisfied for synthesized crystals, h_i was not proportional to SSFE for natural crystal. We propose an idea of "γ center", which correspond to Wulff's point for ideal equilibrium shape crystal. We concluded that, crystal face with the larger SSFE has larger growth rate even for natural crystal.

1   Introduction

Experimental study for specific surface free energy (SSFE) of polymer surface using contact angle of liquid is well known and widely accepted [1-7]. Although the SSFE is significant value to determine the morphology of a single crystal, experimental approach for SSFE of crystal is very few. We performed some experimental trials to determine the SSFE of synthesized ruby [8-10] and chlorapatite [11-14] crystals, and reported that the crystals satisfy Wulff's relationship, that is, SSFE is proportional to the growth rate of the crystals. We also determined the SSFE of synthesized quartz crystal [10]. Though the synthesized quartz crystal is not equilibrium shape and large (more than 200 mm in length), the SSFE and the growth rate of the quartz crystal has a liner relationship: the face with larger growth rate has the larger SSFE. This time, we adopted our experimental technique for natural quartz crystals, and we are going to discuss the relationship between the SSFE and the morphology of natural quartz crystals.

2   Experimental

Sample crystals were carefully produced from a large cluster of crystals with base rock using a diamond saw. We used only the crystals which were found in the deep inside of the cluster where nobody could touch previously. Basically natural quartz crystal has three kinds of faces, r, m, and z faces, as shown in figure 1. We used two bi-pyramidal crystals (Sichuan, China) and two single pyramidal crystals (Diamantina, Brazil), and named BP-1, BP-2, SP-1, and SP-2, respectively. The crystals were sonicated with ethanol and well dried. Droplet of water or formamide was dropped on each face of crystals using a micropipet. The droplets sized ~ 0.1 mm^3 were observed using a digital camera (Nikon COOLPIX 910) with a magnifying lens (Nikon 8×20D). The details of the measurement are described elsewhere [8,9,12,14]. We took more than 200 photographs for each crystal face and used the photographs in which the boundary between the liquid and solid was clearly recognized. The contact angles of the droplets were measured manually using a protractor and printed photographs.

3   Results

The contact angles for the water and formamide droplets had a wide distribution on each face of the crystal. The difference between the maximum and minimum angles for each individual angle was almost 20°. Such

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wide distribution of the contact angle was almost equal to the results for synthesized crystals, like ruby or chlorapatite [8-14]. The average values and standard deviations of contact angles of water and formamide on the crystals BP-1 and BP-2 are summarized in table 1, and the contact angles on the crystals SP-1 and SP-2 are summarized in table 2.
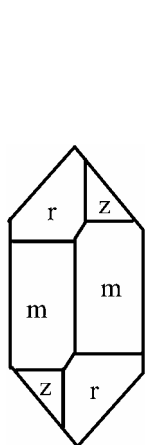
Fig. 1 Faces of natural quartz crystal.
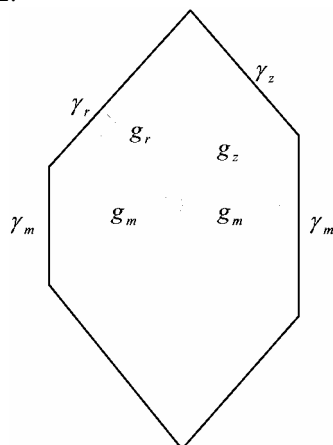
Fig. 2 Schematic picture of the determination of "γ center".
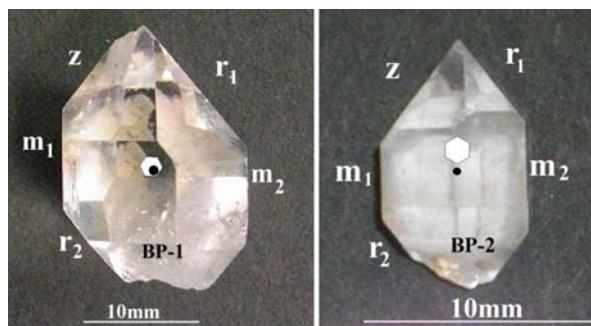
Fig. 3 Natural quartz (BP-1), (BP-2) and their faces. White hexagons are the γ centers, black circles are geometrical centers of the crystals. (Online color at www.crt-journal.org)

Table 1 Average and standard deviation of contact angle of water and formamide on m, r, z faces of tow bi-pyramidal natural quartz crystals. SSFE's calculated using the contact angles are also shown.

crystals	faces	contact angles (degree)		SSFE(mN/m)
		water	formamide	
BP-1	m1	30±5	37±5	60±4
	m2	21±3	15±4	69±1
	r1	35±5	21±5	62±3
	r2	37±4	25±5	61±3
	z	18±4	25±4	61±3
BP-2	m1	38±5	29±5	60±3
	m2	34±5	24±4	63±3
	r1	35±4	27±5	62±3
	r2	50±5	32±5	54±3
	z	40±5	32±4	59±3

Table 2 Average and standard deviation of contact angle of water and formamide on m, r, z faces of tow bi-pyramidal natural quartz crystals. SSFE's calculated using the contact angles are also shown.

crystals	faces	contact angles (degree)		SSFE(mN/m)
		water	formamide	
SP-1	m1	27±5	19±4	66±3
	m2	36±6	25±5	62±4
	r	37±4	21±4	62±2
	z	38±5	22±5	61±3
SP-2	m1	51±4	28±7	54±3
	m2	44±4	28±5	57±3
	r	44±5	20±5	59±3
	z	31±5	21±3	64±3

4   Discussion

Calculation of SSFE   The values of SSFE, γ_S, can be obtained from the contact angle of the liquid, θ, using the Fowkes approximation [1] and Wu's harmonic mean equations [2] as

$$\gamma_{LV}\left(1+\cos\theta\right) = 4\left(\frac{\gamma_{LV}^d \gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p \gamma_S^p}{\gamma_{LV}^p + \gamma_S^p} \right), \tag{1}$$

where γ_{LV} is the surface tension of the liquid, γ_S^d and γ_S^p are the dispersion and polar components of the SSFE of the solid, respectively, and γ_{LV}^d and γ_{LV}^p are those of the surface tension of the liquid, respectively. These equations are widely accepted for use in studies on the SSFE of polymer surfaces [3,4] or inorganic systems such as mica [5,6] and silica [7]. Also our previous experimental results for some inorganic oxide crystals were calculated using this equation and provided reasonable values of SSFE, which satisfies Wulff's relationship. The polar and dispersed components of the liquid were γ_{LV}^d =22.1 mN/m, γ_{LV}^p =50.7 mN/m for water and γ_{LV}^d =39.5 mN/m, γ_{LV}^p =18.7 mN/m for formamide, which were taken from reported data [3]. The calculated SSFE were approximately 54-69 mN/m, as shown in table 1 and 2. Brace and Walsh observed surface energy of quartz by introducing a single flat crack into a quartz crystal (Obreimoff-Gilman method) and reported as 400-1000 mN/m [15]. Their surface energy is more than ten times of our obtained SSFE. However, the surface energy by Obreimoff-Gilman method is not the surface energy of as grown surface, but the energy of breaking the atomic bonds in the bulk crystal.

Though the error in the contact angle measurement was within ±1°, the distribution of the contact angle was wide as ±5°, and the distribution of calculated SSFE was large as ±5 mN/m. Such large distribution of contact angles was also observed in our previous study for synthesized crystals [8-14]. If the surface of the crystal is ideally flat and uniform, the SSFE of the surface should be uniquely determined. Therefore, the distribution of SSFE's can be explained by the contribution of step free energy as,

$$\gamma = \gamma_{ter} + \beta L,$$ (2)

where γ_{ter} is ideal SSFE of the terrace, β is the step free energy and L is the length of the step. Because of the difference of step length, even equivalent faces have different value of SSFE.

SSFE of bi-pyramidal quartz crystals   The relationship between the SSFE and the growth rate of ideal equilibrium shape crystal can be described by Wulff's relationship as [16],

$$\gamma_i / h_i = \text{constant},$$ (3)

where γ_i is the SSFE of the i-th (arbitrary) face of the crystal and h_i is the length of the normal line to the i-th face from Wulff's point in the crystal. The crystal growth is considered to start from the center of the crystal or Wulff's point. This relationship was satisfied for synthesized ruby and chlorapatite crystals, size of which is 1-3 mm [8,9,11-14]. Also the SSFE has liner relationship with the growth rate of synthesized quartz crystal [10]. Length of normal line from the geometrical center to the i-th face of crystal, h_i, is measured using the photo of crystals. The SSFE of the i-th face, γ_i, is compared with h_i for the crystal BP-1. They seemed to satisfy Wulff's relationship as, $\gamma_i \propto h_i$. However, such proportional relationship between γ_i and h_i was not obtained for BP-2. According to our previous study for synthesized quartz crystal, the SSFE's of the growing faces, -X, +X, Z, and S faces have linear relationship with the growth rate of the faces. If we draw normal lines with length of proportional to the SSFE from the crystal face to the inside of the crystal, the lines reach to the seed crystal of synthesized quartz crystal. Therefore, the value of γ_i of large crystals such as industrially synthesized quartz or natural crystal indicates the starting point of the crystal growth, and we determined g_i as,

$$\gamma_i / g_i = \text{constant},$$ (4)

instead of h_i. If we choose the appropriate constant, these lines with length of g_i can cross around the same point in the crystal as shown in figure 2. This crossing point is named "γ center". This γ center is equivalent to Wulff's point for BP-1, because γ center for BP-1 is also its geometrical center. On the other hand, if we postulate $\gamma_i / g_i = 11.2$ for BP-2, the lines cross at almost one point and this point is γ center of this crystal as shown in figure 3 by white hexagon. The size of the white hexagon approximately corresponds to error. The geometrical center is shown by black circle. The position of γ center of BP-2 is observed at a little upper than geometrical center of the crystal. The nucleation of bi-pyramidal crystal should be commenced in the middle of solution as shown in figure 4, and the γ center should be the geometrical center while the crystal is growing in the middle of solution. After the adhesion of the crystal to the base rock, the crystal can grow in the direction opposite to the base rock. There the kinetics of crystal growth is kept to satisfy eq. (4), in order to minimize the total surface free energy of the crystal as,
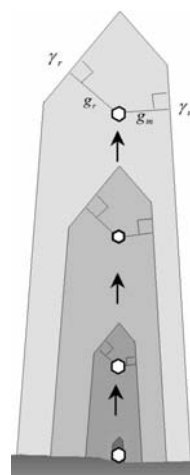
$$G_{surface} = \sum \gamma_i A_i ,$$ (5)

where A_i is the surface area of i-th face. Because the growth of BP-2 is not symmetric, the γ center of BP-2 does not coincide with the geometrical center.
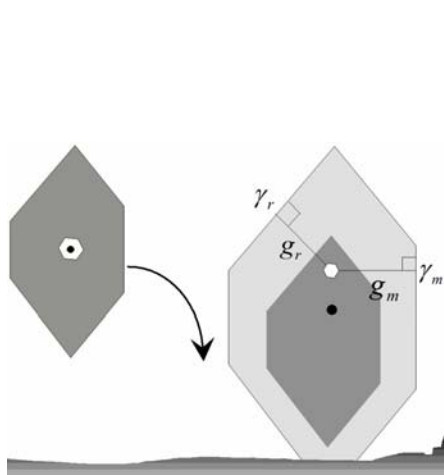
Fig. 4 Schematic picture of growth of bi-pyramidal crystal.

Fig. 5 Natural quartz crystals (SP-1), (SP-2) and their faces. γ centers of SSFE are marked by white hexagons. (Online color)

Fig. 6 Schematic picture of crystal growth and the shift of γ center.

SSFE of single pyramidal quartz crystal γ centers of SP-1 and SP-2 were determined by choosing the constants as $\gamma_i / g_i =$ 12.8 and $\gamma_i / g_i =$ 14.6, respectively, and shown in figure 5 by white hexagons. The γ centers were determined in the upper part of the crystals. The nucleation of single pyramidal quartz crystal should be commenced on the surface of the base rock, and the growing process can be estimated as shown in figure 6. The crystal is always growing in the direction opposite to the base rock, and the γ center should be moving during the crystal growth process. During the each stage of crystal growth, the total surface free energy of the crystal should be kept minimum by the condition of eq. (4). Therefore, the determined γ center means the thermodynamically balanced center for the last stage of crystal growth.

5 Conclusion

Wulff's relationship can be derived by minimization of the total surface free energy of a crystal. If the crystal is small and ideally equilibrium shape, Wulff's relationship can be satisfied as eq. (3) and the crystal grows symmetrically from the nucleation point. On the other hand, growth of natural quartz crystal is not symmetric, because the base rock prevents the symmetric growth. However, the crystal should be growing with the condition of minimum $G_{surface}$. Thermodynamic center of the crystal growth is γ center, and this center moves in order to satisfy the minimization of $G_{surface}$ during the crystal growth. Basically γ center of natural crystal corresponds to the Wulff's point of ideal system.

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