Surface Free Energy and Morphology of Chlorapatite Crystals Grown from Sodium Chloride Flux

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Well-formed crystals of barium chlorapatite [$Ba_5Cl(PO_4)_3$] and strontium chlorapatite [$Sr_5Cl(PO_4)_3$] were grown from a sodium chloride flux. The contact angle of water on the $(10\bar{1}0)$ face of each chlorapatite crystal was observed using a modified Wilhelmy method, where we measured the change of liquid weight instead of the crystal weight. The contact angle depends on the aspect ratio of the crystal. Both the advancing and receding contact angles were larger for $Ba_5Cl(PO_4)_3$ and $Sr_5Cl(PO_4)_3$ crystals with larger aspect ratios. The surface free energy of the $(10\bar{1}0)$ face was calculated using Neumann's equation. The $(10\bar{1}0)$ face of the crystals of larger aspect ratios has a smaller surface free energy, indicating that such crystals have a more stable $(10\bar{1}0)$ face than the crystals of smaller aspect ratios. This result corresponds to the morphology of the chlorapatite crystals because the crystals have a tendency to elongate into the [0001] direction.

The surface free energy is the most significant factor to determine the crystal habit. It is well known that Wulff established the relationship between individual faces of the equilibrium shape and their individual specific surface energies,[1] but we cannot measure the surface free energy directly. There are a lot of theoretical investigations for the calculation of the surface free energy of inorganic crystals. Although there have been a lot of experimental trials to estimate the surface free energy of the organic polymer surfaces,[2–12] the experimental trials for the determination of the surface free energy of an inorganic single crystal have never been performed. To do so, we have experimentally estimated the surface free energy of chlorapatite crystals using the contact angles of water and some organic liquid droplets, and suggested that the morphology of the crystal depends on the surface free energy of each face of the chlorapatite crystals.[13,14] In our previous research,[13,14] we used the static drop method, where we took photos of a liquid droplet on each face of chlorapatite crystals. Though the static drop method directly provides the contact angle of the droplets on the crystal surface, the observed contact angles have very large scatter, e.g., ±8°. We took more than one thousand photos and adopted the most reliable contact angles. The surface of chlorapatite looks very flat by optical microscope measurement, but a lot of defects were observed by atomic force microscope (AFM) measurement. Such local roughness causes the large scatter of the contact angle of the liquid on the crystal surface.[2–4] In this work, we propose a modified Wilhelmy method in order to obtain the average value of the contact angles of water on the crystal surface.

Experimental

Sample Crystals. Crystals of $Ba_5Cl(PO_4)_3$ and $Sr_5Cl(PO_4)_3$ were synthesized using NaCl flux.[15,16] The shapes of both apatite crystals are similar, and they have hexagonal prisms with pyramidal end faces. A schematic representation of the apatite crystal is shown in Fig. 1. The Miller indices of the crystal faces were determined using X-ray diffraction and interfacial angle measurements. The indices of the prismatic faces were $(10\bar{1}0)$, $(01\bar{1}0)$, $(\bar{1}100)$, $(\bar{1}010)$, $(0\bar{1}10)$, and $(1\bar{1}00)$. These six faces are equivalent and the whole collection of these equivalent faces is indicated as $\{10\bar{1}0\}$. We use the symbol $(10\bar{1}0)$ as a representative when we refer to a specific face of these equivalent faces. The twelve pyramidal faces were also equivalent and belong to the form $\{10\bar{1}1\}$. We use the symbol $(10\bar{1}1)$ for a specific face of these equivalent faces. The crystals have the tendency to elongate in [0001] and $[000\bar{1}]$ directions. These directions are indicated by the symbol $\langle 0001 \rangle$. The length L (parallel to the $\langle 0001 \rangle$ directions), and width, W (perpendicular to the $\langle 0001 \rangle$ directions), of the crystals were measured by optical microscope observation. The aspect ratios are determined as L/W. The densities of $Ba_5Cl(PO_4)_3$ and $Sr_5Cl(PO_4)_3$ crystals were determined pycnometrically, and they were 4.80 and 4.09 $g\,cm^{-3}$, respectively. The sizes of the crystals used for the experiment were 0.6–0.9 mm in width and 1.6–3.0 mm in length.

Measurement of Contact Angle. Figure 2 shows a schematic representation of the measurement of the force between water and the chlorapatite crystal. We measured the weight of the liquid instead of the weight of the crystal and we call this method a modified Wilhelmy method. The chlorapatite crystal was suspended on the bottom of a micrometer with stainless steel wire. The [0001] direction is parallel to the vertical line. A glass vessel with distilled water was settled on an electric balance. The effect of the evaporation of water was calibrated as the constant weight loss

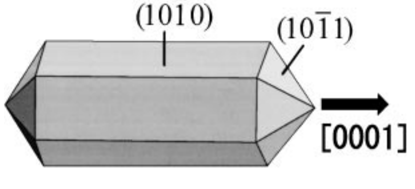

Fig. 1. The morphology of $Ba_5Cl(PO_4)_3$ or $Sr_5Cl(PO_4)_3$ crystal.

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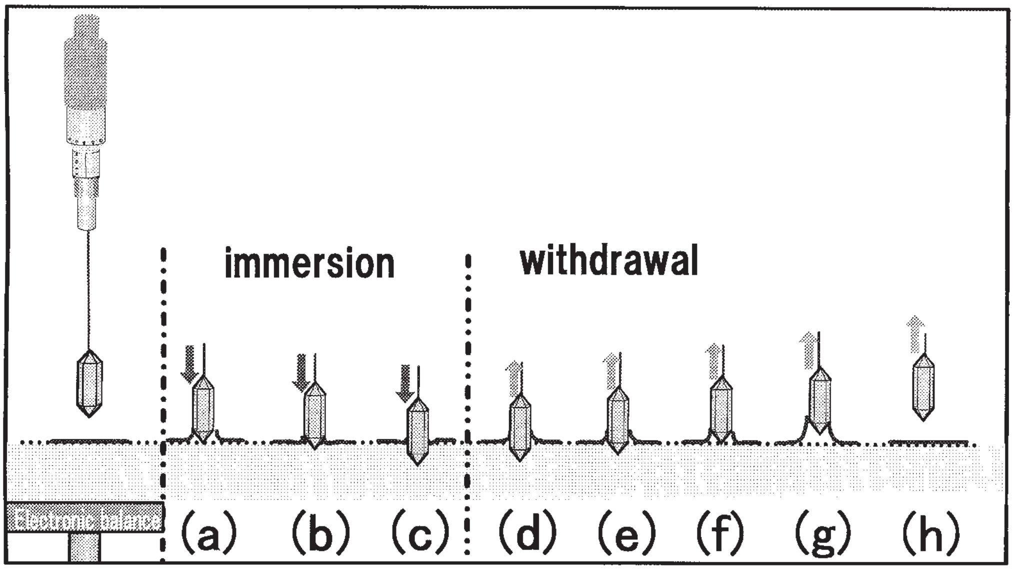

Fig. 2. Schematic representation of the measurement of the contact angle of the water surface to the $(10\bar{1}0)$ face of a chlorapatite single crystal by a modified Wilhelmy method.

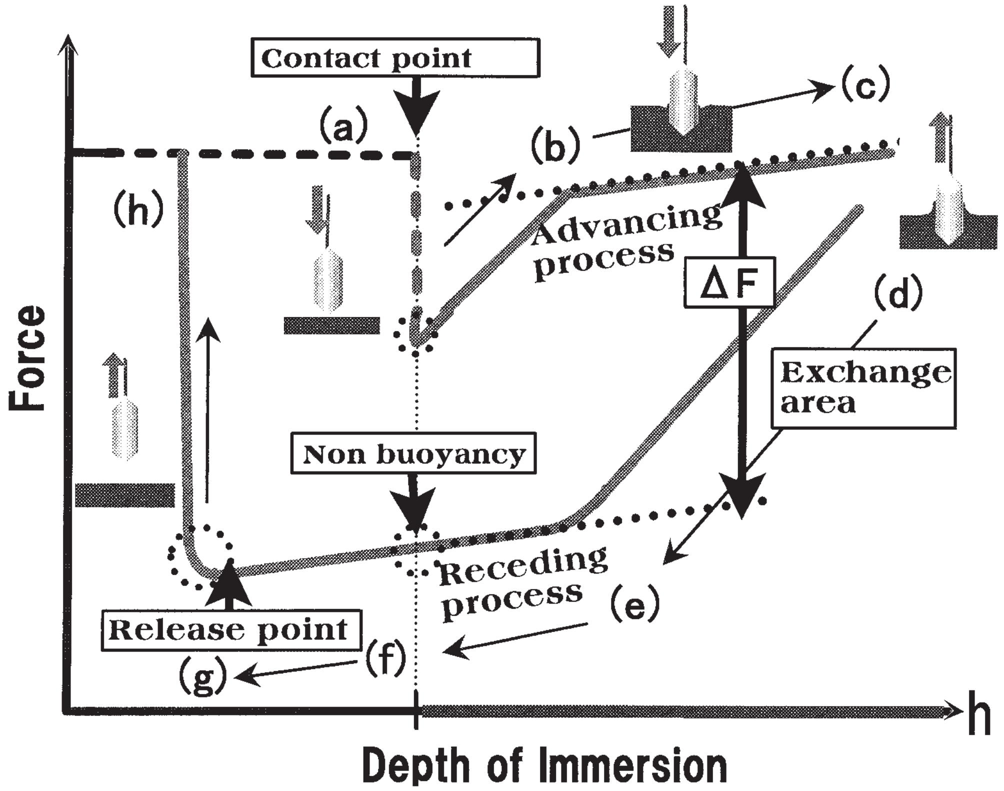

Fig. 3. Schematic representation of an ideal hysteresis loop of the interfacial force by a modified Wilhelmy method.

during a cycle of the measurement. The indication of the electric balance is the total weight of water and the glass vessel, the reaction of buoyancy, and the interface force between the crystal surface and liquid. An ideal hysteresis loop of the force as a function of the immersion depth of the crystal is shown in Fig. 3. This force can be obtained by subtraction of the weight of the liquid and the vessel from the indication of the electric balance. The crystal approaches the surface of water and it touches the surface at point (a) and the surface of water is pulled up by the surface tension. From point (b) to point (c) the surface of water forms a stable meniscus, and the force between the crystal and the liquid can be described as

$$F_A = sh\rho g - P\gamma_L \cos\theta_A, \quad (1)$$

where s is the cross section, ρ is the density of the liquid, h is the depth of immersion, g is the gravity constant, P is the perimeter of the crystal, γ_L is the surface tension of water, and θ_A is the advancing contact angle. $sh\rho g$ is the buoyancy term in this equation.

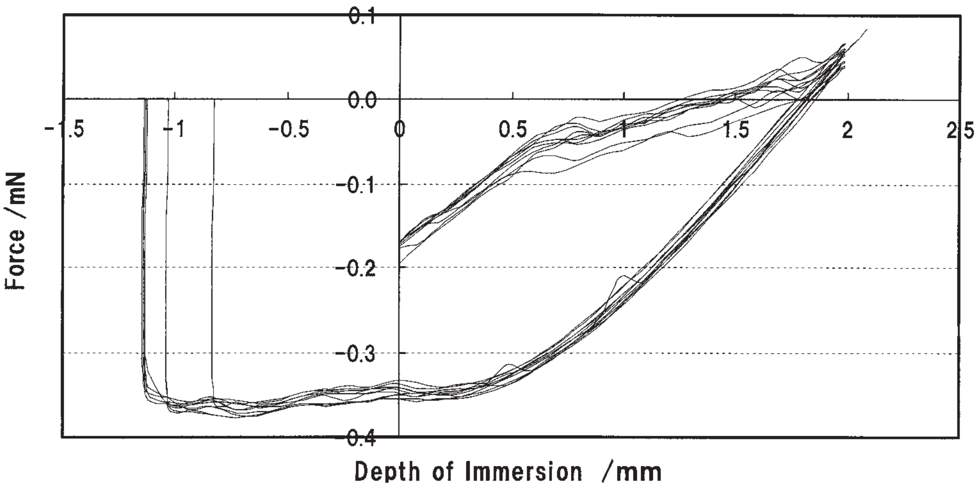

Fig. 4. Hysteresis loops of the force between the water surface and $(10\bar{1}0)$ face of the $Ba_5Cl(PO_4)_3$ crystal.

The force was measured at every 0.1 mm of h. At each measuring point, the sample was kept for at least 20 s, then the indication of the electric balance became constant. We measured the static contact angle at each point. At point (c), the crystal was pulled up. The force became smaller because the contact angle of water changes from the advancing to receding process between points (d) and (e). The difference of the force (ΔF) between points (d) and (e) is given by the following equation:

$$\Delta F = F_A - F_R = P\gamma_L(\cos\theta_R - \cos\theta_A), \tag{2}$$

where θ_R is the receding contact angle. The force of the receding process, from (e) to (g), is determined and shown as

$$F_R = sh\rho g - P\gamma_L\cos\theta_R. \tag{3}$$

The slope of the line between (e) and (g) gives $s\rho g$. Because ρ and g are known, the cross section of the crystal, s, can be obtained. Point (f) is the same depth as point (a), where no buoyancy operates to the crystal and the force can be shown as the following equation.

$$F_R^0 = -P\gamma_L\cos\theta_R. \tag{4}$$

The perimeter, P, can be geometrically calculated from the cross section, s, postulating that the crystal has an ideal hexagonal cross section. Using Eq. 4, the absolute value of θ_R can be calculated. When θ_R is substituted in Eq. 2, we obtain the advancing contact angle, θ_A.

Results

Experimental hysteresis loops of the force of water and $Ba_5Cl(PO_4)_3$ crystals are shown in Fig. 4. In this figure, we show ten trials of the measurement for the same $Ba_5Cl(PO_4)_3$ crystal. The aspect ratio of this crystal is 2.0. The lines of the advancing and receding process are not straight, but have slight curvatures. However, the reproducibility of the lines of the hysteresis loops are very good; therefore, the line shape indicates the surface property. Using the hysteresis loops in Fig. 4, we can estimate the slope of the advancing and receding process. The surface tension of water, γ_L, is 72.8 mJ m^{-2}.[10] The slope gives the cross section of the crystal, s, using Eq. 1, and s is 3.3 mm^2 for this sample. The perimeter, P, can be geometrically calculated from s, and the value of θ_R can be calculated using Eq. 4, giving $\theta_R = 59.9°$. The value of θ_A can be calculated using Eq. 2 as $\theta_A = 82.1°$. We also measured θ_A and θ_R for different samples, of which the aspect ratios were 1.2 and 2.7. Figure 5 shows the contact angles of the water on the $(10\bar{1}0)$ face of $Ba_5Cl(PO_4)_3$ crystals as a function of the aspect ratios. Though θ_A does not have enough dependence on the aspect ratio of the crystals, the receding contact angles have significant dependence on the aspect ratio, indicating that the crystals with large aspect ratios have large contact angles. We also measured θ_A and θ_R by the modified Wilhelmy method for $Sr_5Cl(PO_4)_3$ crystals of different aspect ratios, as shown in Fig. 6. Although they gave some scatter, the θ_R has obvious dependence on the aspect ratio, as that of $Ba_5Cl(PO_4)_3$ crystals.

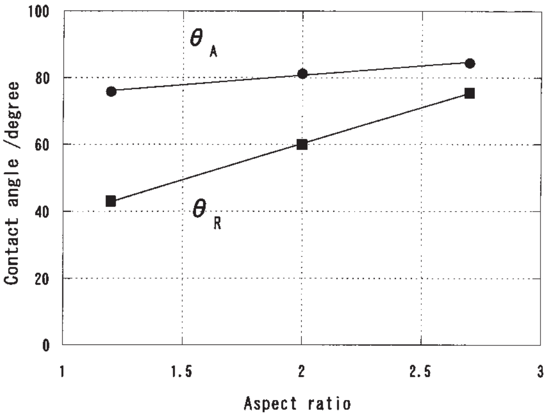

Fig. 5. Advancing (θ_A) and receding (θ_R) contact angles of water to the $(10\bar{1}0)$ face of the $Ba_5Cl(PO_4)_3$ crystal as a function of the aspect ratio of the crystal.

Theoretical Background

The relationship between the surface tension and the contact angle is indicated by Young's equation as the following:

$$\gamma_{SL} + \gamma_L\cos\theta = \gamma_S, \tag{5}$$

where γ_S, γ_L, γ_{SL}, and θ are the surface tension of the solid that corresponds to the surface free energy, surface tension of liquid, interface tension of the solid and liquid, and contact angle, respectively. This equation indicates that the contact angle reflects the surface tension of the solid. Though we cannot

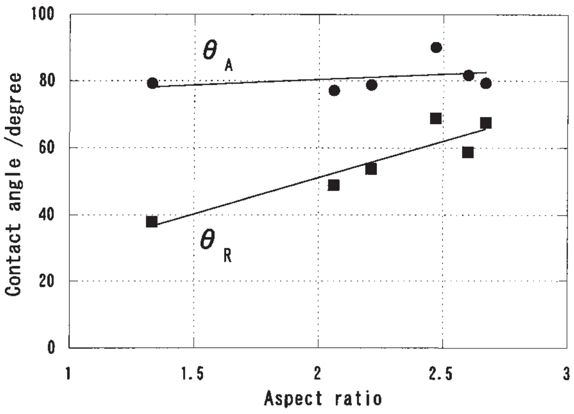

Fig. 6. Advancing (θ_A) and receding (θ_R) contact angles of water to the $(10\bar{1}0)$ face of the $Sr_5Cl(PO_4)_3$ crystal as a function of the aspect ratio of the crystal.

directly observe the value of γ_{SL}, we can calculate γ_S using Neumann's equation,[5–9]

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L \gamma_S}\exp(-\beta(\gamma_L - \gamma_S)^2), \qquad (6)$$

where β is a constant. This constant is known for a polymer as 0.0001247 $(m^2\,mJ^{-1})^2$.[5–9] We need to determine this constant for chlorapatite. Combining Eq. 6 with Eq. 5 yields

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_L}}\exp(-\beta(\gamma_L - \gamma_S)^2). \qquad (7)$$

In this equation, only the surface tension of the solid, γ_S, is unknown, and it is a function of the contact angle, θ.

Discussion

Although Neumann's equation is very convenient, because we can calculate γ_S from the contact angle, the constant β was only given for the polymer surface[5–9] and that for the inorganic solid surface is unknown. We have already adopted Eq. 6 in order to obtain the surface free energy of round shaped $Ba_5Cl(PO_4)_3$ and $Sr_5Cl(PO_4)_3$ crystals from the contact angle of water using the β of the polymer surface.[13] The absolute value of the surface free energy was not reliable, but qualitatively it gave a reasonable explanation for the relationships between the surface free energy and the morphology of the crystals. Therefore, this time, we calculated β for the chlorapatite surface. In our previous research,[14] we have measured the contact angles of water, formamide, ethyleneglycol, and diethyleneglycol droplets on the faces of $Ba_5Cl(PO_4)_3$ crystals, and obtained the surface free energy of the $(10\bar{1}0)$ face of $Ba_5Cl(PO_4)_3$ crystals as $\gamma_S = 58\,mN\,m^{-1}$ when the contact angle of water was 40°,[14] using the harmonic mean equation.[10–12] The aspect ratio of the crystals used for the static drop method was 1.1–1.3. In order to measure the contact angle of a liquid using the static drop method, we need a rather large crystal, and it is difficult to use a needle-like crystal for the measurement of contact angle. β for the chlorapatite can be estimated by Eq. 7 with the value of $\gamma_S = 58\,mN\,m^{-1}$, which was obtained by the static drop method,[14] and β was found to be 0.0000510 $(m^2\,mJ^{-1})^2$. The surface free energies of $Ba_5Cl(PO_4)_3$ and $Sr_5Cl(PO_4)_3$ crystals were calculated using Eq. 7 by substituting the calibrated β and the measured contact angles calculated by Eq. 6 are shown in Fig. 7 and Fig. 8. The relationship between γ_S and the aspect ratio of the chlorapatite crystal is obvious: When the crystal becomes longer, the surface free energy, γ_S, becomes smaller. It may be possible to say vice versa. The crystals with small γ_S can become long crystal. Regardless, if the γ_S of the $(10\bar{1}0)$ face is small, the large surface area of $(10\bar{1}0)$ may be energetically favorable for crystal growth. In our previous research, using crystals of small aspect ratio we found that the γ_S of the $(10\bar{1}0)$ face is smaller than that of the $(10\bar{1}1)$ face of the chlorapatite crystal, which corresponds to the morphology of the chlorapatite crystal, because the crystals have a tendency to elongate into [0001] direction.[13,14] Then, we needed to put a small droplet of liquid on the faces of $(10\bar{1}0)$ and $(10\bar{1}1)$ in order to directly measure the contact angle wish a digital camera. On the other hand, we used needle-like crystals in this research. Their $(10\bar{1}1)$ faces are very small and impossible to place a droplet onto. However, the needle-like crystals have a large or long

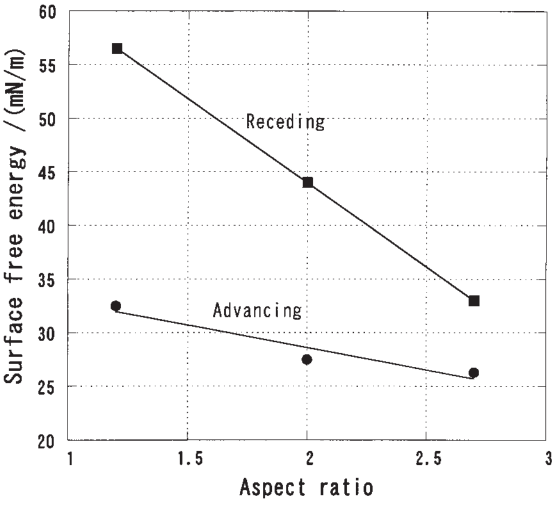

Fig. 7. Surface free energy (γ_S) of the $(10\bar{1}0)$ face of the $Ba_5Cl(PO_4)_3$ crystal as a function of the aspect ratio of the crystal.

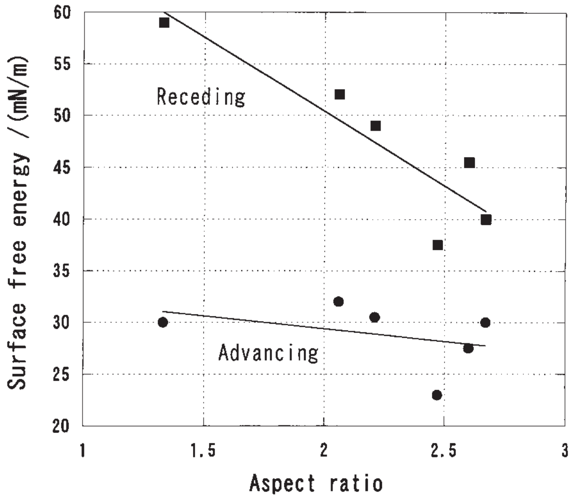

Fig. 8. Surface free energy (γ_S) of the $(10\bar{1}0)$ face of the $Sr_5Cl(PO_4)_3$ crystal as a function of the aspect ratio of the crystal.

enough $(10\bar{1}0)$ face, and they are advantageous for Wilhelmy method measurement. The θ_R by this modified Wilhelmy method for a crystal of small aspect ratio is close to the contact angle of a water droplet on the chlorapatite crystals observed by the static drop method.[14] We observed the contact angle of a water droplet on round shaped $Ba_5Cl(PO_4)_3$ crystals, of which the aspect ratio was 1.1–1.3 by the static drop method.[14] The average of the observed contact angle of water on the $(10\bar{1}0)$ face was 40°, which is close to the θ_R for a small aspect ratio in Fig. 5. Since we used very small droplets of 0.2 µL in the static drop method, the water was vaporizing during the observation, and we might have measured the θ_R of the water droplet on the crystal by the static drop method.

All of the crystals we used in this experiment look very flat by optical microscope observation. If the surface of the crystal is perfectly flat, they should not have any dependence on the aspect ratios, because they would be chemically the same. The roughness of atomic size may cause the difference of the surface free energy. The step of the crystal surface has step free energy, and it is considered to increase the observed surface free energy of the crystal. We also observed the crystal surface using atomic force microscopy (AFM), and we could observe the roughness of the crystal surface. However, the roughness distributes randomly on the surface, and it depends on the position where one observes. It was impossible to obtain quantitative information of the whole single face. As it is well known, if the surface is perfectly flat, θ_A and θ_R should be equal. If we elongate the lines of θ_A and θ_R or γ_S of Figs. 5–8, they cross at the point where aspect ratio is about 4. This aspect ratio may give ideally a perfect single crystal.

Conclusion

Though the static drop method provides the contact angle of several kinds of liquids, the shape of the crystal is limited to round shaped crystals. Also, it is necessary to take many pictures, for example more than one thousand, in order to obtain the average of the contact angles. On the other hand, the Wilhelmy method provides the average value of the contact angle of water on the $(10\bar{1}0)$ face of needle-like chlorapatite single crystals and it also gives the advancing and receding contact angles, separately. The Wilhelmy method also has a limitation for the size or the shape of the objective crystals. We could measure the contact angles of water on the $(10\bar{1}0)$ face, but not that on the $(10\bar{1}1)$ face. The combination of this modified Wilhelmy method with the static drop method provides useful information for the surface free energy of single crystals, and it will support the theoretical research of crystallography.

In this work, we proposed a modified Wilhelmy method. Of course, when we used an ordinal Wilhelmy method, it gave the same result. However, this modified Wilhelmy method does not need a special apparatus: An ordinal electric balance and a micrometer are enough to measure the contact angle. It is simple and less expensive.

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