Surface Tension of Barium Chlorapatite Crystals Grown from Flux

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Large, well-formed crystals of barium chlorapatite [$Ba_5Cl(PO_4)_3$] were grown from a sodium chloride flux. The prismatic crystals of $Ba_5Cl(PO_4)_3$ were bordered by $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ faces. The crystals have a tendency to elongate in the $\langle 0001 \rangle$ directions. Contact angles of water, formamid, ethylene glycol, and diethylene glycol droplets on the $Ba_5Cl(PO_4)_3$ crystals were observed. The surface tension, that is, the surface free energy of the grown crystals, was calculated in order to study the relationship between the morphology and the surface tension of the crystal. The contact angles of water, formamid, ethylene glycol, and diethylene glycol droplets on the $(10\bar{1}0)$ face of a $Ba_5Cl(PO_4)_3$ crystal were 40°, 37°, 30°, and 26°, respectively, and the contact angles of those liquids on the $(10\bar{1}1)$ face were 20°, 18°, 16°, and 14°, respectively. The surface tension of the crystal faces were calculated from the observed contact angles using harmonic mean and geometric mean equations. The calculated surface tensions of the crystal faces were 58 ± 1 and 69 ± 1 mN/m for the $(10\bar{1}0)$ and $(10\bar{1}1)$ faces of a $Ba_5Cl(PO_4)_3$ crystal, respectively. The fact that the surface tension of the $(10\bar{1}0)$ face is smaller than that of the $(10\bar{1}1)$ face indicates that the $(10\bar{1}0)$ face is more stable than the $(10\bar{1}1)$ face. The energetic stability of the $(10\bar{1}0)$ face corresponds to the morphology of the $Ba_5Cl(PO_4)_3$ crystal, which elongates in the $\langle 0001 \rangle$ directions.

Large, well-formed crystals of barium chlorapatite [$Ba_5Cl(PO_4)_3$] were grown from a sodium chloride flux for the first time by Oishi et al.[1] The prismatic crystals of $Ba_5Cl(PO_4)_3$ form $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ faces, and the crystals have a tendency to elongate in the $\langle 0001 \rangle$ directions. The morphology of the $Ba_5Cl(PO_4)_3$ crystals depends on the solute content in NaCl flux. For example, long prismatic crystals were grown when mixtures containing 0.4–1.8 mol% of solute were used. On the other hand, when mixtures containing 1.9–2.2 mol% solute were used, short prismatic crystal were grown.[1] The relationship between the solute content and the mechanism of crystal growth is still unknown. We have also grown $Sr_5Cl(PO_4)_3$[2] and $CaMoO_4$ crystals[3] from a NaCl flux. Our interest is to develop a technique to grow large and well-formed single crystals from a NaCl flux. We are also trying to control the morphology of the flux grown crystals. As the mechanism of crystal growth from a NaCl flux has not been studied, we gave attention to the surface tension, that is, the surface free energy of the grown crystals. The nature of the crystal growth should depend on the thermodynamic stability of each face of the crystal. Because the morphology of a crystal is determined by the stability of each face, several trials were performed to explain the growth mechanism of crystals by calculating the surface energy of a single crystal.[4] Therefore the experimental measurement of the surface free energy of a single crystal of inorganic oxide is important. However, because of the absence of surface mobility, a solid surface is very different from a liquid surface. We cannot directly measure the surface tension of a solid surface. Therefore, theoretical calculations are useful approach to study the surface tension of a single crystal. For example, the surface energies of single crystals of gibbsite[4] or some metals[5] have been calculated for faces with different Miller indices and the relationship with the morphology discussed. At this time, there are no experimental or theoretical studies for the surface energy of chlorapatite crystals. To do so, experimental trials to measure the surface tension of a solid polymer surface is performed using contact angles of liquid droplets.[6–13] There are also many theoretical trials to investigate the contact angle of liquids on polymer surfaces.[5,6,10,14] In this work, we adopted an established experimental contact angle measurement method for the determination of the surface tension of a polymer surface in order to study the surface tension of $Ba_5Cl(PO_4)_3$ crystals.

Experimental

Sample Crystals. Crystals of $Ba_5Cl(PO_4)_3$ were synthesized using a NaCl flux.[1] Reagent-grade $(NH_4)_2HPO_4$, $BaCO_3$, $BaCl_2{\cdot}2H_2O$, and NaCl were used for the flux growth of $Ba_5Cl(PO_4)_3$ crystals. A mixture of $6(NH_4)_2HPO_4 + 9BaCO_3 + BaCl_2{\cdot}2H_2O$ powders was used as a solute and NaCl powder was used as the flux. A mixture containing 1.2 mol% solute was prepared, as the largest $Ba_5Cl(PO_4)_3$ crystal has been obtained at this solute content.[1] The mixture was put into a platinum crucible. The crucible was heated to 1100 °C at a rate of about 45 °C/h, held at this temperature for 10 h, and then cooled to 500 °C at a rate of 5 °C/h. When the cooling process was completed, the crucible was allowed to cool down to room temperature. The crystalline products were separated by dissolving the flux in warm water. The $Ba_5Cl(PO_4)_3$ crystals are hexagonal prisms with pyramidal end faces. A schematic representation of the $Ba_5Cl(PO_4)_3$ 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

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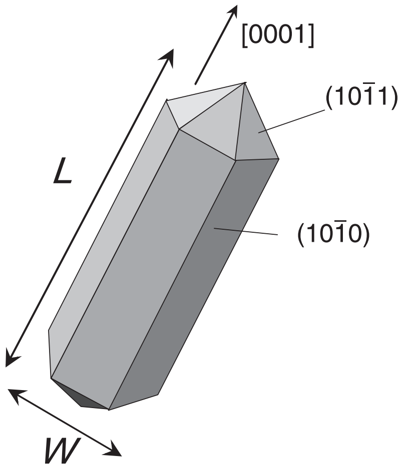

Fig. 1. Schematic picture of $Ba_5Cl(PO_4)_3$ crystal.

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 mention a specific face of these equivalent faces. The twelve pyramidal faces were also equivalent and belong to the form $\{10\bar{1}0\}$. We use the symbol $(10\bar{1}1)$ for a specific face of these equivalent faces. The crystals have the tendency to elongate in the [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 using an optical microscope. The sizes of the crystals were approximately less than 3 mm in length and less than 0.5 mm in width. The aspect ratios (L/W) for $Ba_5Cl(PO_4)_3$ crystals we used in this experiment were 1.1–4.2.

Measurement of the Contact Angle of Liquid. The crystals were sonicated with ethanol and well dried. The crystals were fixed on a glass plate using a small bit of clay. The sample liquid was dropped on the crystal using a micropipet. The volume of the liquid droplet was 0.2 mm^3. The droplet was observed using a digital camera (Nikon COOLPIX 910) with a magnifying lens (Nikon 8 × 20D). Figures 2 and 3 show photographs of a droplet of distilled water and diethylene glycol on the edge between the $(10\bar{1}0)$ and $(10\bar{1}1)$ faces of a $Ba_5Cl(PO_4)_3$ crystal, respectively. The crystals were so small that it was difficult to settle a droplet onto a single face of the crystal. The contact angle of the droplet on the $(10\bar{1}0)$ face is referred to as θ_0, and that on the $(10\bar{1}1)$ face as θ_1. Because the droplet is not on a simple and large flat surface, we could not use a well-established video based sessile drop method. In addition, the crystal is transparent, and the boundary between the liquid and crystal is not clear. We took many photographs and chose ones on which we could recognize the boundary between the liquid and solid. The contact angles, θ_0 and θ_1, were measured manually using a graduator and printed photographs. In order to avoid a subjective bias, we measured the contact angles, θ_0 and θ_1, more than 30 times for the same crystal and observed 20 crystals of $Ba_5Cl(PO_4)_3$. Holding the crystal at several angles against the horizontal plane, the droplet was observed in order to investigate the influence of gravity on the shape of the droplet. The liquid droplets we used in this experiment were so small that the contact angle did not depend on the slope of the crystal face.

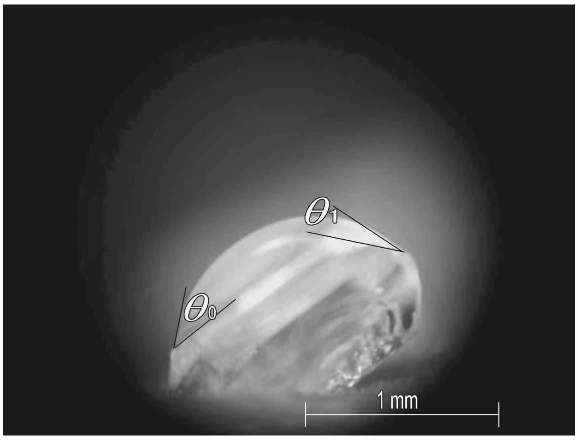

Fig. 2. A photograph of water droplet on the edge between the $(10\bar{1}0)$ and $(10\bar{1}1)$ faces of $Ba_5Cl(PO_4)_3$ crystal. The contact angles of liquid sample with $(10\bar{1}0)$ and $(10\bar{1}1)$ faces are determined as θ_0 and θ_1, respectively.

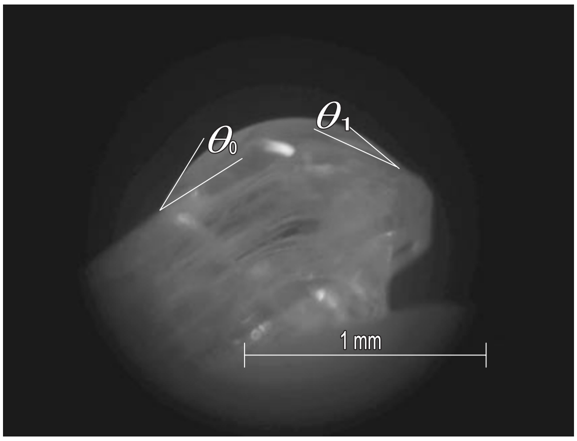

Fig. 3. A photograph of diethylene glycol droplet on the edge between the $(10\bar{1}0)$ and $(10\bar{1}1)$ faces of $Ba_5Cl(PO_4)_3$ crystal.

Theoretical Background

The relationship between surface tension and the contact angle of a liquid is shown by Young's equation:[15]

$$\gamma_{SL} + \gamma_{LV}\cos\theta = \gamma_S \tag{1}$$

where γ_S is the surface energy of the solid, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_{LV} is the surface tension of the liquid. We adopted harmonic and geometric means in order to obtain the surface energy, γ_S. It was proposed by Wu,[16] and it is widely accepted, that the intermolecular energy between two materials results from the summation of a dispersion component and a polar component.[17] Although this estimation was proposed for the analysis of the surface tension of a polymer surface, we adopted this method for this study. The intermolecular energy between the liquid and inorganic solid consists of the dispersion and polar component, like a system of a liquid and polymer solid. The surface tension γ can be obtained as a sum of the dispersion component and the polar component. The interfacial tension between a liquid and a solid can be evaluated by the harmonic mean equation, as follows:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 4\left(\frac{\gamma_{LV}^{d}\gamma_S^{d}}{\gamma_{LV}^{d} + \gamma_S^{d}} + \frac{\gamma_{LV}^{p}\gamma_S^{p}}{\gamma_{LV}^{p} + \gamma_S^{p}}\right) \tag{2}$$

or the geometric mean equation, as follows:

Table 1. Dispersion (γ^{d}) (mN/m) and Polar (γ^{p}) (mN/m) Component of Surface Tension (γ) at 20 °C of the Liquids Used in This Work

Liquid	γ^{d}	γ^{p}	γ
Water	22.1	50.7	72.8
Formamide	39.5	18.7	58.2
Ethyleneglycol	30.1	17.6	47.7
Diethyleneglycol	31.7	12.7	44.4

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{S}} + \gamma_{\mathrm{LV}} - 2\big((\gamma^{\mathrm{d}}_{\mathrm{LV}}\gamma^{\mathrm{d}}_{\mathrm{S}})^{1/2} + (\gamma^{\mathrm{p}}_{\mathrm{LV}}\gamma^{\mathrm{p}}_{\mathrm{S}})^{1/2}\big) \tag{3}$$

where $\gamma^{\mathrm{d}}_{\mathrm{S}}$ and $\gamma^{\mathrm{p}}_{\mathrm{S}}$ are the dispersion and polar components of the surface energy of the solid, and $\gamma^{\mathrm{d}}_{\mathrm{LV}}$ and $\gamma^{\mathrm{p}}_{\mathrm{LV}}$ are the dispersion and polar components of the surface tension of the liquid. The values of $\gamma^{\mathrm{d}}_{\mathrm{LV}}$ and $\gamma^{\mathrm{p}}_{\mathrm{LV}}$ for the liquids we used in this work were fond in the literature[17] and summarized in Table 1. Equations 2 and 3 can be transformed into Eq. 4 (harmonic mean) and 5 (geometric mean), respectively.

$$\gamma_{\mathrm{LV}}(1+\cos\theta) = 4\left(\frac{\gamma^{\mathrm{d}}_{\mathrm{LV}}\gamma^{\mathrm{d}}_{\mathrm{S}}}{\gamma^{\mathrm{d}}_{\mathrm{LV}}+\gamma^{\mathrm{d}}_{\mathrm{S}}} + \frac{\gamma^{\mathrm{p}}_{\mathrm{LV}}\gamma^{\mathrm{p}}_{\mathrm{S}}}{\gamma^{\mathrm{p}}_{\mathrm{LV}}+\gamma^{\mathrm{p}}_{\mathrm{S}}}\right) \tag{4}$$

$$\gamma_{\mathrm{LV}}(1+\cos\theta) = 2\big((\gamma^{\mathrm{d}}_{\mathrm{LV}}\gamma^{\mathrm{d}}_{\mathrm{S}})^{1/2} + (\gamma^{\mathrm{p}}_{\mathrm{LV}}\gamma^{\mathrm{p}}_{\mathrm{S}})^{1/2}\big) \tag{5}$$

We can solve Eqs. 4 or 5 using the contact angle of two liquids in Table 1.

Results and Discussion

The measured contact angles of water droplets on $\mathrm{Ba_5Cl(PO_4)_3}$ crystals are summarized in Fig. 4. Because the measurement of the contact angle contains some error, the values are listed within a scatter of 2 degrees. As shown in Fig. 4, the contact angle of a water droplet on the $(10\bar{1}0)$ face, θ_0, was observed to be 40° most frequently, but the scatter of the observed angles was large. The smallest value of θ_0 was 24° and the maximum value of θ_0 was 48°. The contact angle on the $(10\bar{1}1)$ face, θ_1, observed most frequently was around 20°, also with a wide scatter: $14° \le \theta_1 \le 42°$. Although the synthesized $\mathrm{Ba_5Cl(PO_4)_3}$ crystals have very flat surface, as seen in the SEM photographs,[1] the crystals do have some defects or atomic scale roughness on the surface. This atomic scale roughness may give rise to the large scatter of the values of the contact angles of the sample liquids on the $\mathrm{Ba_5Cl(PO_4)_3}$ crystals. It is well known that the contact angle of a liquid on a solid surface depends on the roughness of the surface.[9,18] However, so far, we cannot evaluate the roughness of the crystal surface.

θ_0 and θ_1 for a formamide droplet on $\mathrm{Ba_5Cl(PO_4)_3}$ crystals are shown in Fig. 5. The center of the distribution of θ_0 was 37°, and that of θ_1 was 18°. Though they had a wide scatter, $20° \le \theta_0 \le 44°$, and $12° \le \theta_1 \le 36°$, we can say that θ_0 is much larger than θ_1. Both contact angles, θ_0 and θ_1, can be said to be smaller than those for water.

Figure 6 shows θ_0 and θ_1 for an ethylene glycol droplet on $\mathrm{Ba_5Cl(PO_4)_3}$ crystals. The center of the distribution of θ_0 was 30°, and the scatter was $20° \le \theta_0 \le 40°$. The distribution of θ_1 had a center at 16°, and the scatter was $8° \le \theta_1 \le 38°$. θ_0 was larger than θ_1, as other liquid samples. Both θ_0 and θ_1 for ethylene glycol were smaller than those of water or formamide.

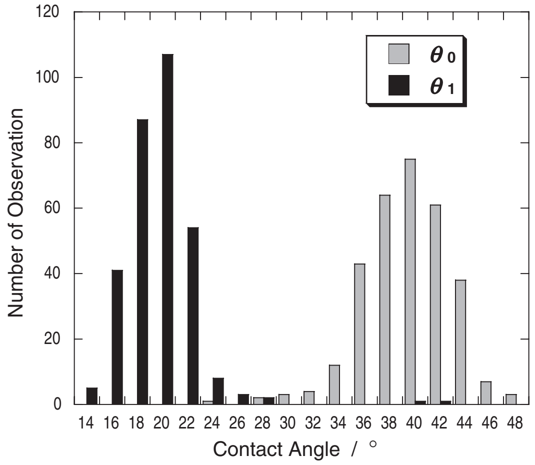

Fig. 4. The number of observation of contact angles θ_0 and θ_1 for water droplet on $\mathrm{Ba_5Cl(PO_4)_3}$ crystals.

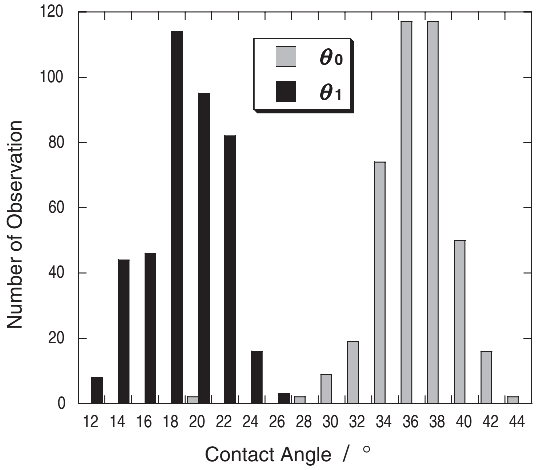

Fig. 5. The number of observation of contact angles θ_0 and θ_1 for formamid droplet on $\mathrm{Ba_5Cl(PO_4)_3}$ crystals.

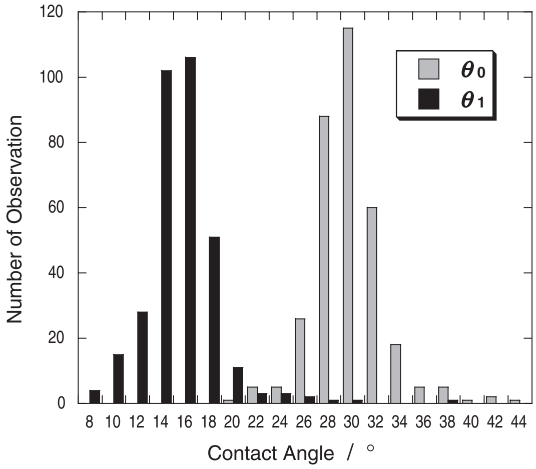

Fig. 6. The number of observation of contact angles θ_0 and θ_1 for ethylenglycol droplet on $\mathrm{Ba_5Cl(PO_4)_3}$ crystals.

Table 2. Surface Tension γ_S (mN/m) and Its Dispersion γ_S^d (mN/m) and Polar γ_S^p (mN/m) Component at 20 °C for $(10\bar{1}0)$ Face of $Ba_5Cl(PO_4)_3$ Crystal Calculated by Harmonic and Geometric Mean Equation

Pair of liquids	Harmonic			Geometric		
	γ_S^d	γ_S^p	γ_S	γ_S^d	γ_S^p	γ_S
Water–Diethyleneglycol	18	40	58	9.4	49	58
Water–Ethyleneglycol	14	44	58	41	23	64
Water–Formamide	22	36	58	16	41	57

Table 3. Surface Tension γ_S (mN/m) and Its Dispersion γ_S^d (mN/m) and Polar γ_S^p (mN/m) Component at 20 °C for $(10\bar{1}1)$ Face of $Ba_5Cl(PO_4)_3$ Crystal Calculated by Harmonic and Geometric Mean Equation

Pair of liquids	Harmonic			Geometric		
	γ_S^d	γ_S^p	γ_S	γ_S^d	γ_S^p	γ_S
Water–Diethyleneglycol	19	50	69	6.7	68	75
Water–Ethyleneglycol	15	55	70	3.8	75	79
Water–Formamide	25	44	69	16	53	69

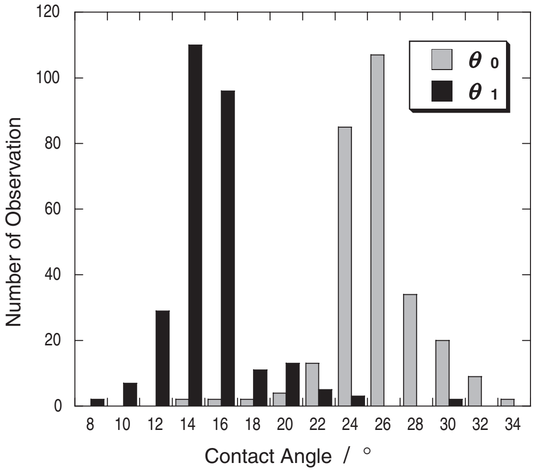

Fig. 7. The number of observation of contact angles θ_0 and θ_1 for diethylenglycol droplet on $Ba_5Cl(PO_4)_3$ crystals.

Figure 7 shows θ_0 and θ_1 for diethylene glycol. The center of the distribution of θ_0 was 26°, and that of θ_1 was 14°. The scatters of θ_0 and θ_1 were $14° \le \theta_0 \le 34°$ and $8° \le \theta_1 \le 30°$, respectibely. It can be concluded that θ_0 is larger than θ_1 for diethylene glycol, as for the other sample liquids. We can also say that both θ_0 and θ_1 are the smallest of all liquid samples observed in this experiment.

The order of the contact angles is, from largest to smallest, water > formamide > ethylene glycol > diethylene glycol, for both θ_0 and θ_1. The larger the surface tension of the liquid, the larger the contact angle. In order to calculate the surface tension of the crystal surfaces, we adopted the contact angles of water, formamide, ethylene glycol, and diethylene glycol droplets on the $(10\bar{1}0)$ face, θ_0, of as 40°, 37°, 30°, and 26°, respectively, and the contact angles on the $(10\bar{1}1)$ face, θ_1, as 20°, 18°, 16°, and 14°, respectively. The surface tension of the $(10\bar{1}0)$ and $(10\bar{1}1)$ faces were calculated using the values in Table 1 and the harmonic (Eq. 4) or geometric mean equations (Eq. 5), and are summarized in Tables 2 and 3, respectively. The values calculated by the harmonic mean equation had better agreement than the values calculated by the geometric mean equation for both θ_0 and θ_1. The harmonic mean equation gives surface tensions with an error of ±1 mN/m if we adopt the center of the distributions of the contact angles shown in Figs. 4–7. According to the harmonic mean equation, the surface tensions for the $(10\bar{1}0)$ face (γ_{S0}), and that of the $(10\bar{1}1)$ face (γ_{S1}) are as 58 ± 1 mN/m and 69 ± 1 mN/m, respectively. That is, the $(10\bar{1}0)$ face is energetically more stable than the $(10\bar{1}1)$ face. The crystals of $Ba_5Cl(PO_4)_3$ have a tendency to elongate into the $\langle 0001 \rangle$ directions, indicating that the crystals increase the surface area of the $(10\bar{1}0)$ face more than the area of the $(10\bar{1}1)$ face. Of course, the absolute values of the surface tension of crystals at the temperature of the crystal growth may be different from the surface tension at room temperature. However, the $Ba_5Cl(PO_4)_3$ crystal belongs to the hexagonal system, and it does not have a phase transition between the temperature of the crystal growth and room temperature. Therefore, the energetic relationship between each face of the grown crystals measured at room temperature should be applicable for the evaluation of the mechanism of crystal growth.

Conclusion

An obvious difference between the contact angles of water, formamide, ethylene glycol, and diethylene glycol droplets on the different faces of $Ba_5Cl(PO_4)_3$ was observed. The surface tension of the different faces of a $Ba_5Cl(PO_4)_3$ crystal was calculated by considering the dispersion and polar components of the surface tensions to obtain the relationship $\gamma_{S0} < \gamma_{S1}$, which reflects the morphology of the $Ba_5Cl(PO_4)_3$ crystal.

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