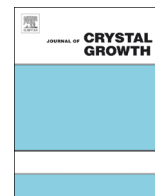




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ABSTRACT

Each XRD peak intensity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals changes according to their morphologies. This research clarifies the relationship between XRD peak intensity and morphologies on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals synthesized by reaction crystallization with various additives. As a result, as XRD relative intensity of (021) face increases, average longitude and aspect ratio decrease and needle-like or plate-like large crystals transform into granular microcrystals.

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1. Introduction

Polymorphs are substances with same chemical composition, which have various crystal structures. Morphologies are fundamentally different among polymorphs due to a difference of crystal phase, resulting in a difference of X-ray diffraction (XRD) charts. In addition, each polymorph has peculiar thermodynamically stable zone because physical and chemical properties are different among polymorphs. Meanwhile, crystal habit is a difference of crystal shape resulting from the difference of growth rate of each crystal face. Growth rates of equivalent crystal faces can be different according to reaction conditions though targets are identical substances with the same number of constituent faces and identical ideal forms, resulting in a difference of crystal habit. Although crystal shape and crystal size are different among crystals showing different crystal habits, XRD peak positions are identical because chemical compositions, physical properties and chemical properties are identical among them. However, intensities of each diffraction peak are different among them because total area of each crystal face is different according to crystal habit.

Crystal morphology of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ changes according to reaction conditions such as additives, pH, and reaction time. At the same time, intensity of each XRD peak also changes.

This phenomenon is assumed to be one example of crystal habit and some interesting relationship may exist between morphology and XRD peak intensity on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. However, few studies correlate morphology with XRD peak on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, so the detail of the relationship between them remains unclear.

This study aims to clarify the detailed relationship between crystal morphology and XRD peak intensity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In this study, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals showing various morphologies were synthesized by reaction crystallization with various additives chosen randomly. Morphology (crystal shape, average longitude and aspect ratio), absolute intensity and relative intensity of major XRD peaks on synthesized $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were examined and relationships between them were clarified. Moreover, crystal growth mechanism and crystal structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were discussed by analyzing crystal size, XRD absolute intensity and XRD relative intensity. Crystal structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Miller index of each crystal face have been defined by several authors [1,2], however, some Miller indices defined by them does not correspond with JCPDS or major peaks on XRD charts. Therefore, crystal structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Miller index of each crystal face are worthwhile to investigate.

We focused on five major diffraction peaks: (020), (021), (130), (041), and (-221). Positions (2θ) of these peaks are 11.6° , 20.7° , 23.4° , 29.1° , and 31.1° , respectively. Miller indices of these peaks were referred to PDF#00-033-0311. Concerning $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals synthesized from raw material solutions with appropriate concentrations without additives, their typical morphologies are needle-like or plate-like, and (020) diffraction peak is much stronger than any other peaks. XRD absolute intensities of other diffraction faces are usually negligibly low.

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2. Experiment

This research examines the relationship between crystal morphology and XRD absolute or relative intensity, crystal structure and Miller index of each crystal face on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

In this research, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals showing various morphologies were synthesized by reaction crystallization with various additives. Additives were chosen randomly among acids, bases, inorganic salts, organic compounds, and polyelectrolytes. CaCl_2 solution and Na_2SO_4 solution were used as raw materials. Concentration and volume of raw materials were basically standardized as 0.3 mol/L and 50 mL respectively. Exceptionally, concentrations of raw materials were increased to 0.6–1.5 mol/L when using additives which can increase solubility or can suppress nucleation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Experimental conditions are shown in Table 1. Reaction crystallization was carried out at room temperature.

200 mL of deionized water or additive solution was put into 300 mL beaker reactor and agitated by magnetic stirrer. 50 mL of CaCl_2 solution and 50 mL of Na_2SO_4 solution with predetermined concentrations were added in order. Through this operation $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was formed. Formed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was ripened in agitating condition or static condition for predetermined duration. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals were separated from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ slurry by suction filtration, and dried in oven at 40 °C for more than 24 h.

After drying, crystal morphology (crystal shape and crystal size) was observed by optical microscope (VH-Z450, KEYENCE). Average longitude (major axis), average latitude (minor axis), crystal size distribution, coefficient of variation (CV) and aspect ratio were calculated from micrographs. Crystallinity of each product was analyzed by XRD (Rint-Ultima III, Rigaku). XRD absolute intensity (crystallinity) was determined from the strongest diffraction peak. XRD relative intensity was calculated by defining XRD intensity of (020) peak, ordinarily the strongest peak, as 100. Morphology, XRD absolute intensity and XRD relative intensity of synthesized $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were examined and the relationships between them were discussed.

3. Results and discussions

XRD relative intensities of major peaks on (020) peak were varied with additives. Especially, relative intensity of (021) peak on (020) peak was varied the most widely from under 10 to over 100.

Therefore, the relationship between crystal morphology and XRD relative intensity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was examined by classifying results into four types according to XRD relative intensity of (021) peak: (1) 0–10, (2) 10–20, (3) 20–50, (4) 50–100 and more than 100. Experimental results organized from the view of XRD relative intensity of (021) peak are shown in Tables 2 and 3. Examples of micrographs and XRD charts are shown in Figs. 1 and 2, respectively.

3.1. Crystal habits caused by additives

3.1.1. Detailed characteristics of crystals classified by XRD relative intensity of (021) peak

The case XRD relative intensity of (0 2 1) peak is 0–10 occurred when adding concentrated citric acid, HCl or citric acid in static condition, or using concentrated raw materials' solutions with acidified PEI. In these cases, needle-like or plate-like large crystals with large aspect ratio were dominant. Especially in static conditions, coarse crystals whose longitude reached to hundreds of micrometer or millimeter order were formed. These results were assumed to be led by slow and precise growth resulting from solubility increase by acidic additives. In the case of using acidified PEI, large crystals were formed by rapid but stable growth resulting from high concentration of raw materials in the presence of PEI behaving as stabilizer. In contrast, when using concentrated citric acid, irregular plate-like or wide plate-like crystals with relatively small aspect ratio were dominant. This result indicates high concentration of citric acid have an effect to change crystal habit by preventing crystal growth along longitude direction. Similarly-shaped microcrystals or granular microcrystals assumed to be broken crystals or secondary crystals were also observed in these cases. Coexistence of coarse crystals and microcrystals degraded CV especially in the case using HCl in static condition.

The case XRD relative intensity of (021) peak is 10–20 occurred when adding PVP, PEI, NaCl, or using no additives. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals synthesized from raw material solutions with appropriate concentrations without additives correspond to this case (Fig. 1(e)), in other words, this case, XRD relative intensity of (021) peak is 10–20, is the most popular on reaction crystallization of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In these cases, needle-like or plate-like large crystals with large aspect ratio and some microcrystals formed together similarly to the case XRD relative intensity of (021) peak is 0–10. Coarse crystals were

Table 1
Experimental conditions. Reaction crystallization was carried out at room temperature.

Series	Raw materials						Ripening time after nucleation	
	CaCl_2		Na_2SO_4		Additives		Deionized	
	Concentration [mol/L]	Volume [mL]	Concentration [mol/L]	Volume [mL]	Type	Amount	water [mL]	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reagent	–	–	–	–	–	–	–	
Without additives	0.3	50	0.3	50	–	–	200	
Without additives (ripened for 5 min)	0.3	50	0.3	50	–	–	200	
HCl (Static)	0.9	50	0.9	50	35% HCl	10 mL	200	
NaOH	0.3	50	0.3	50	1 mol/L NaOH	0.3 mL	200	
NaCl (ripened for 1 day)	0.3	50	0.3	50	NaCl	2 g	200	
Concentrated citric acid	0.9	50	0.9	50	Citric acid	100 g	200	
Citric acid (Static)	0.3	50	0.3	50	Citric acid	2 g	200	
Urea	0.3	50	0.3	50	Urea	2 g	200	
PEI	0.3	50	0.3	50	15 g/L PEI70000	200 mL	–	
Acidified PEI (concentrated raw materials)	1.5	50	1.5	50	10 g/L PEI70000	200 mL	–	
PVP	0.3	50	0.3	50	35% HCl	10 mL	–	
PAA250000	0.6	50	0.6	50	10 g/L PVP	200 mL	–	
CMC-Na	0.9	50	0.9	50	1 g/L PAA250000	200 mL	–	
					10 g/L CMC-Na	200 mL	–	

Table 2
Experimental results (XRD absolute intensity and XRD relative intensity to (020) diffraction face).

XRD relative intensity of (021) face [%]	Series	XRD absolute intensity					XRD relative intensity to (020) face				
		(020) [cps]	(021)	(130)	(041)	(-221)	(020) [%]	(021)	(130)	(041)	(-221)
0–10	Acidified PEI (concentrated raw materials)	43575	2153	4826	3707	369	100	4.9	11.1	8.5	0.8
	Concentrated citric acid	16028	1528	2881	2753	431	100	9.5	18.0	17.2	2.7
	Citric acid (Static)	33059	2159	5606	2818	228	100	6.5	17.0	8.5	0.7
	HCl (Static)	65558	6533	15722	6714	97	100	10.0	24.0	10.2	0.1
	0–10 average	39555	3093	7259	3998	281	100	7.7	17.5	11.1	1.1
10–20	Without additives	27557	3213	3492	5046	569	100	11.7	12.7	18.3	2.1
	PEI	11883	2215	2623	2833	904	100	18.6	22.1	23.8	7.6
	PVP	17430	2926	2163	3959	513	100	16.8	12.4	22.7	2.9
	NaCl (ripened for 1 day)	32365	4044	5820	4104	272	100	12.5	18.0	12.7	0.8
20–50	10–20 average	22309	3100	3525	3986	565	100	14.9	16.3	19.4	3.4
	CaSO ₄ ·2H ₂ O reagent	12598	2664	1830	2988	894	100	21.1	14.5	23.7	7.1
	Without additives (ripened for 5 min)	10470	2705	2201	3280	598	100	25.8	21.0	31.3	5.7
	NaOH	7928	2522	1370	3204	770	100	31.8	17.3	40.4	9.7
	Urea	12375	3363	2457	4320	793	100	27.2	19.9	34.9	6.4
50–100	20–50 average	10843	2814	1965	3448	764	100	26.5	18.2	32.6	7.2
	PAA250000	2693	2093	476	1352	1386	100	77.7	17.7	50.2	51.5
100–	CMC-Na	2142	2906	384	1984	1388	100	135.7	17.9	92.6	64.8

Table 3
Experimental results (Crystal shape, crystal size and aspect ratio).

XRD relative intensity of (021) face [%]	Series	Crystal shape	Longitude		Latitude		Aspect ratio	
			Average [μm]	CV [dimension less]	Average [μm]	CV [dimension less]	Average [dimension less]	CV [dimension less]
0–10	Acidified PEI (concentrated raw materials)	needle, indefinite plate or granular	12.96	0.672	4.41	0.924	4.15	0.878
	Concentrated citric acid	indefinite plate or granular	11.06	0.698	5.56	0.892	2.46	0.527
	Citric acid (Static)	needle or indefinite plate	100.78	0.858	28.98	0.757	4.08	0.678
	HCl (Static)	needle or granular	40.24	1.797	8.52	0.682	5.51	1.649
	0–10 average	coarse needle or coarse plate	41.26	1.006	11.87	0.814	4.05	0.933
10–20	Without additives	needle or plate	17.27	0.447	3.52	0.808	7.29	0.741
	PEI	plate or granular	11.47	0.624	3.47	0.619	3.62	0.494
	PVP	needle, indefinite plate or granular	6.46	0.554	2.43	0.674	3.24	0.653
	NaCl (ripened for 1 day)	needle	18.45	0.871	3.12	0.710	7.74	1.069
20–50	10–20 average	needle or plate	13.41	0.624	3.13	0.703	5.47	0.739
	CaSO ₄ ·2H ₂ O reagent	granular or indefinite plate	7.58	0.799	3.33	1.008	2.72	0.555
	Without additives (ripened for 5 min)	broken needle or broken plate	4.07	0.502	1.37	0.554	3.57	0.680
	NaOH	broken needle or granular	7.77	0.447	2.00	0.649	5.34	0.812
	Urea	needle, plate or granular	3.42	0.585	1.11	0.559	3.43	0.649
50–100	20–50 average	needle, plate or granular	5.71	0.583	1.95	0.692	3.77	0.674
	PAA250000	granular or aggregated	2.38	0.490	1.20	0.445	2.06	0.359
100–	CMC-Na	granular	2.21	0.520	1.17	0.475	1.99	0.426

formed only in the case using NaCl, however, this result is mainly ascribed to longer ripening time (1 day).

The case XRD relative intensity of (021) peak is 20–50 occurred when adding NaOH or urea, or the case ripened 5 min without additives. In these cases, granular crystals as well as plate-like or needle-like crystals were formed. Both average longitude and aspect ratio of these crystals were smaller than the cases XRD relative intensity of (021) peak is 0–10 and 10–20. These results were assumed to be led by following mechanisms: slow growth resulting from solubility increase and growth suppression by urea, mass nucleation and minimization of crystals resulting from solubility decrease by NaOH, or insufficient growth resulting from shorter ripening time. In these cases, broken crystals and chipped crystals

were also included, which suggests durability of crystals is decreased. Although secondary particles were certainly included, it was difficult to distinguish between them from originally-small crystals. CaSO₄·2H₂O reagent also corresponded to this case, however, it showed unique morphology: thick and coarse granular crystals.

The cases XRD relative intensity of (021) peak are 50–100 and more than 100 occurred when adding PAA250000 or CMC-Na, respectively. Both additives were polyelectrolytes having carboxyl groups. In these cases, morphology of synthesized CaSO₄·2H₂O dramatically changed from needle-like or plate-like large crystals to granular microcrystals, whose average size was about 2.3 μm. These results were assumed to be led by slow growth rate resulting from nucleation suppression and/or solubility increase

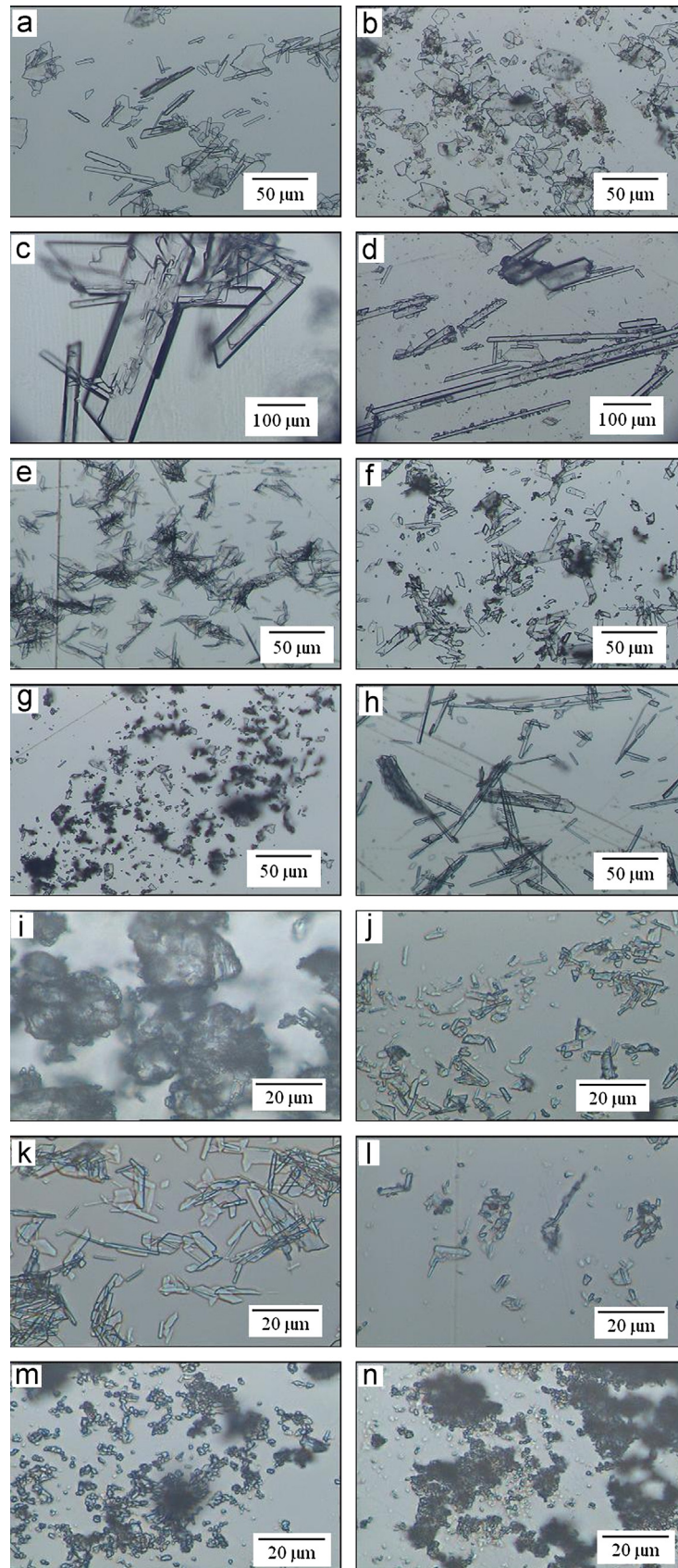


Fig. 1. Micrographs of crystals. (a)–(d) XRD relative intensity of (021) peak is 0–10. (e)–(h) XRD relative intensity of (021) peak is 10–20. (i)–(l) XRD relative intensity of (021) peak is 20–50. (m)–(n) XRD relative intensity of (021) peak is 50–100 and more than 100. (a) Acidified PEI (concentrated raw materials) (b) Concentrated citric acid (c) Citric acid (static). (d) HCl (static) (e) Without additives (f) PEI (g) PVP (h) NaCl (ripened for 1 day). (i) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reagent (j) Without additives (ripened for 5 min) (k) NaOH (l) Urea. (m) PAA250000 and (n) CMC-Na.

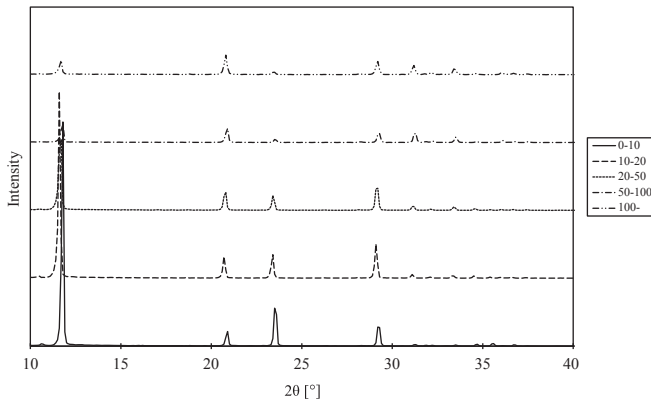


Fig. 2. Examples of XRD charts whose XRD relative intensity of (021) peak is 0–10, 10–20, 20–50, 50–100, and more than 100. As XRD relative intensity of (021) peak increased, XRD absolute intensities of (020) peak and (130) peak decreased and that of (–221) peak increased.

by polyelectrolytes, and growth suppression resulting from steric hindrance of polyelectrolytes and electrostatic interaction between Ca atom and carboxyl groups of polyelectrolytes. It was impossible to distinguish between primary crystals and secondary crystals, broken crystals and originally-small crystals. In addition, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ impurities were included in these cases.

3.1.2. Interaction mechanism between $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals and additives

In this research, aspect ratio of synthesized crystals dramatically decreased when using concentrated citric acid, PAA250000 and CMC-Na; additives having carboxyl groups. This result indicates that crystal growth along longitude direction is suppressed by the interaction between carboxyl groups of additives and crystal growth point on latitude of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals. If such interactions exist, Ca atoms should locate on the side surface along latitude direction.

To examine this hypothesis, abundance ratio of S atom to Ca atom (S/Ca) on each crystal surface was newly analyzed by X-ray photoelectron spectroscopy (XPS) (PHI5000 Versa Probe WS, ULVAC-PHI) on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals synthesized without additives. As a result, S/Ca on the side surface along latitude direction was about 0.9. In contrast, S/Ca on the largest surface and on the side surface along longitude direction were more than 1.0. S/Ca on the side surface along latitude direction and those of other crystal surfaces can be considered to differ significantly because abundance of S atom and that of Ca atom in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystal are basically equal. These results mean that Ca atoms are more likely to locate on the side surface along latitude direction of plate-like crystals or at the point of needle-like crystals than any other surface of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals. This tendency will be the same in the presence of additives. Therefore, crystal growth along longitude direction will be suppressed when using additives having carboxyl groups by electrostatic interaction between carboxyl groups of additives and Ca atoms at crystal growth point on the side surface along latitude direction. This interaction will change crystal shape by preserving growth-suppressed surfaces, and as a result, aspect ratio of these crystals will decrease. Moreover, when using polyelectrolytes having carboxyl groups, not only crystal shape change but also crystal size decrease will proceed simultaneously, which will change needle-like or plate-like large crystals into granular microcrystals. Concerning additives that will not interact electrostatically with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals, they will adsorb equally to each surface of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals and will not affect their crystal shapes.

3.2. Relationships among XRD absolute intensity, XRD relative intensity and crystal morphology

3.2.1. The relationship between XRD absolute or relative intensity and crystal size

The relationships between XRD absolute or relative intensity and longitude are shown in Figs. 3 and 4.

As longitude increased, XRD absolute intensity of (020) face and (130) face increased exponentially (Fig. 3). This result suggests (020) face and (130) face are parallel to longitude. In contrast, XRD absolute intensity of (–221) face decreased exponentially as longitude increased. This result suggests (–221) face grows rapidly and disappears as crystal grows along longitude direction. XRD absolute intensities of (021) face and (041) face were hardly affected by longitude increase, in other words, they were kept nearly constant regardless of longitude. This result suggests (021) face and (041) face are vertical to longitude. Because XRD absolute intensity of (021) face and (041) face are kept constant, these peaks outstands when granular microcrystals are dominant. However, XRD absolute intensity of (041) face can be considered to increase slightly as longitude increased. This result suggests (041) face slightly grows under the influence of crystal growth along longitude direction though (041) face is not to be parallel to longitude. The relationship between XRD absolute intensity and latitude was less clear than longitude, however, (020) face, (130) face and (–221) face showed similar tendency to those of longitude. Concerning (021) face and (041) face, relationship to longitude was unclear.

Meanwhile, XRD relative intensity to (020) face decreased exponentially except for (130) face as longitude increased (Fig. 4). This result means the area of (021), (041) and (–221) faces relatively decrease as the area of (020) face increases by crystal growth along longitude direction. In other words, crystal shape changes from granular to needle or plate as the area of (020) face increases. In contrast, XRD relative intensity of (130) face was kept constant. This result ensures the theory that (130) face is parallel to longitude as well as (020) face and these faces grow together. On (–221) face, not only XRD absolute intensity but also XRD relative intensity was correlated with longitude. In fact, XRD relative intensity of (–221) face became larger as granular microcrystals became dominant. This result ensures the theory that (–221) face grows rapidly and disappears as crystal grows along longitude direction. The change of XRD relative intensity against latitude was similar to that against longitude.

Correlation coefficients on the relationships between XRD absolute or relative intensity and crystal size were 0.7 at best. This is because XRD absolute intensity depends not on representative length but on the surface area of each diffraction face.

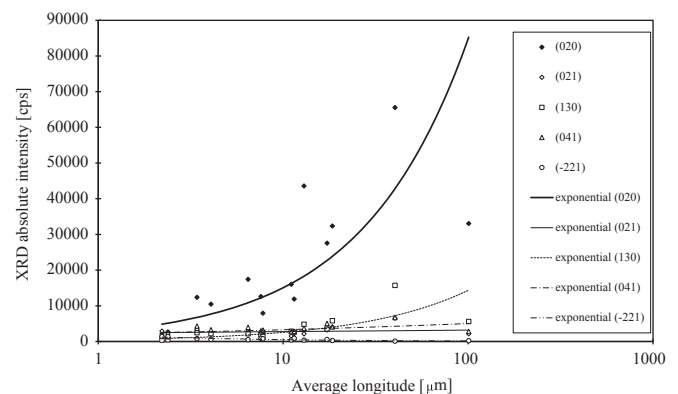


Fig. 3. The relationship between average longitude and XRD absolute intensity. Exponential approximate equations of each diffraction face are as follows: (020): $y = 2676.2x^{0.7504}$, $R^2 = 0.6703$, (021): $y = 2387.6x^{0.0632}$, $R^2 = 0.0375$ (130): $y = 457.61x^{0.7477}$, $R^2 = 0.6788$, (041): $y = 2158.4x^{0.1841}$, $R^2 = 0.2485$ (–221): $y = 1935.9x^{-0.5675}$, $R^2 = 0.6798$.

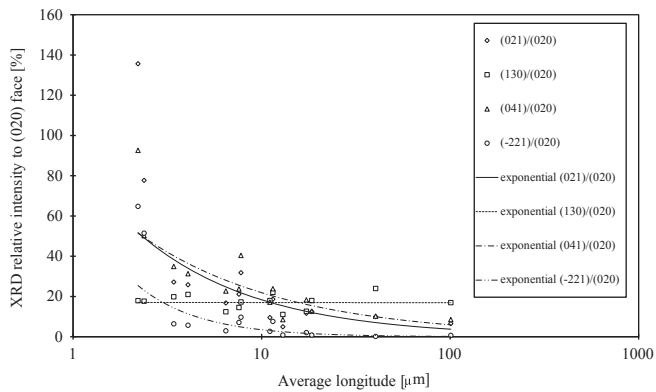


Fig. 4. The relationship between average longitude and XRD relative intensity. Exponential approximate equations of each diffraction face are as follows: (021)/(020): $y = 89.215x^{-0.6872}$, $R^2 = 0.6514$, (130)/(020): $y = 17.099x^{-0.0027}$, $R^2 = 0.0002$ (041)/(020): $y = 80.651x^{-0.5663}$, $R^2 = 0.7522$, (-221)/(020): $y = 72.338x^{-1.3179}$, $R^2 = 0.7163$.

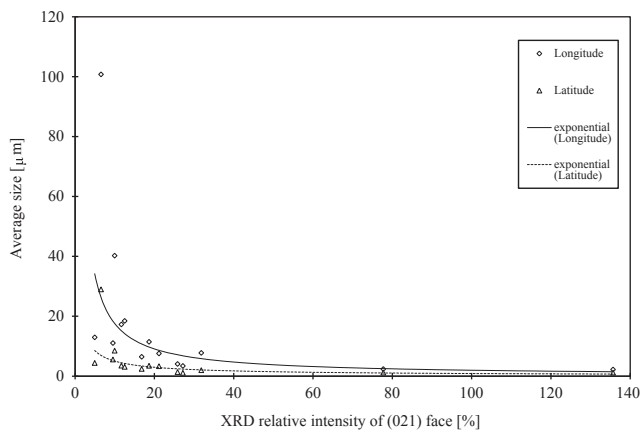


Fig. 5. The relationship between XRD relative intensity of (021) face and average size. Exponential approximate equations of longitude and latitude are as follows: Longitude: $y = 155.58x^{-0.948}$, $R^2 = 0.6514$, Latitude: $y = 28.696x^{-0.7571}$, $R^2 = 0.5888$.

For example, shape of grown crystal can be needle-like or plate-like though surface areas of them are equal. In addition, increase of crystal thickness will be error source.

3.2.2. Relationships between XRD relative intensity of (021) face and crystal morphology, XRD relative intensity of (021) face and that of other faces

The relationships between XRD relative intensity of (021) face and crystal morphology are shown in Fig. 5. Decrease of average longitude and average latitude means that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals become smaller by increase of XRD relative intensity of (021) face. However, because average longitude decreases more rapidly than average latitude, aspect ratio decreases as XRD relative intensity of (021) face increases. As a result, shape of synthesized $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ changes from needle-like or plate-like to granular as XRD relative intensity of (021) face increases. Crystal shape changed the most dramatically when XRD relative intensity of (021) face was around 50.

The relationships between XRD relative intensity of (021) face and XRD relative intensity of each diffraction face are shown in Fig. 6. As XRD relative intensity of (021) face increased, XRD relative intensities of (041) face and (-221) face also increased. On (-221) face, XRD absolute intensity increased as well as XRD relative intensity (Table 2). In contrast, XRD relative intensity of

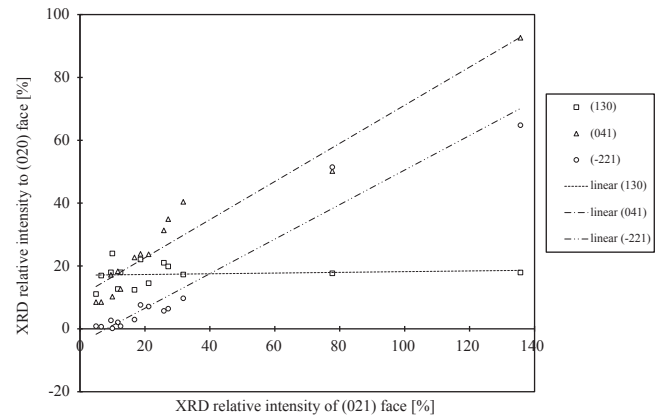


Fig. 6. The relationship between XRD relative intensity of (021) face and those of other faces. Linear approximate equations of each diffraction face are as follows: (130): $y = 0.0113x + 17.055$, $R^2 = 0.0117$, (041): $y = 0.6067x + 10.464$, $R^2 = 0.9387$ (-221): $y = 0.5495x - 4.4445$, $R^2 = 0.9487$.

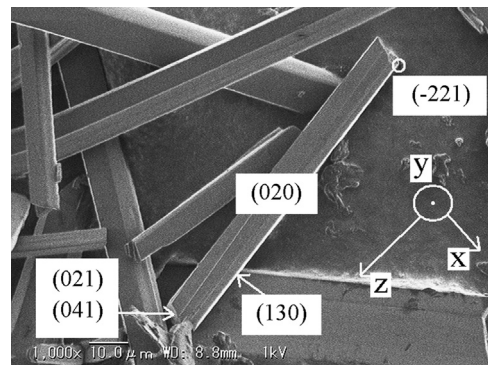


Fig. 7. Assumed crystal axes and crystal faces of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

(130) face kept constant. These changes of XRD relative intensities correspond to morphology changes, in other words, as relative area of (021) face increases, relative areas of (041) face and (-221) face also increase, as a result, synthesized $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ changes from needle-like or plate-like large crystals to granular microcrystals.

3.2.3. Estimation of crystal axis and crystal face of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

From above results, crystal axes and approximate crystal structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are assumed to be as Fig. 7. X–Y–Z coordinate system is defined not to be inconsistent with each crystal face. (020) face is usually largest and the most outstanding face, therefore, longitude and latitude of crystals are usually decided from (020) face. (020) face is parallel to x axis and z axis, and vertical to y axis. (130) face is parallel to z axis similarly to (020) face. This face extends to depth direction, in other words, (130) face has the component of crystal thickness. (021) face and (041) face are vertical to z axis, in other words, these faces are vertical to (020) face and (130) face. However, inclination is different between (021) face and (041) face. (-221) face is assumed to be trace level in Fig. 7. This face is assumed to exist at the corner of crystal because this face is not parallel to any axes. This face outstands only at the beginning of crystal growth or in the case that granular microcrystals are dominant, and disappears rapidly as crystal grows along longitude direction. Other crystal faces showing low XRD absolute intensity may appear at edge or corner of crystal, however, they will not affect approximate crystal structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

4. Conclusion

XRD relative intensity of each diffraction face on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ changes according to crystal morphology. As XRD relative intensity of (021) face increases, XRD relative intensities of (041) face and (-221) face also increase. At the same time, average longitude and aspect ratio decrease and needle-like or plate-like large crystals transform into granular microcrystals. In addition, XRD absolute intensity and XRD relative intensity on particular crystal faces are correlated with longitude. However, correlate coefficients are 0.7 at best because XRD absolute intensity is depend not on representative length but on total area of each diffraction face.

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Appendix A

CMC-Na: sodium carboxymethylcellulose.
CV: coefficient of variation.
PAA: polyacrylic acid.
PEI: polyethyleneimine.
PVP: polyvinylpyrrolidone.
XPS: X-ray photoelectron spectroscopy.
XRD: X-ray diffraction.

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