

## Collectivity and individuality of particle dispersion under gravity

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Collective motion of fine particles in liquid can be widely seen not only in engineering processes but also in natural phenomena such as water treatment [1], sediment transport [2], bio-convection [3] and lava convection [4]. It is well-known that the spatial variance of particle concentration brings about large-scale convection flow under gravity and sometimes it affects macroscopic motion of particles. In this study, of particular interest is whether collective or individual motion of particles reveals in liquid under the gravity field. The existence of concentration interface, which is an ambiguous interface between suspended particles and pure fluid, plays a significant role in these extreme behaviors.

Figure indicates the settling behaviors of stratified-suspended particles in a vertical Hele-Shaw cell filled with liquid [5]. In cases of small particle size with high concentration, the interfacial instability occurs at the lower concentration interface and the suspended particles behave as an immiscible fluid even though there is no distinct border with pure fluid [6]. Consequently the settling velocity is much faster than that of an isolated particle. On the other hand, in case of large particles with low concentration, the concentration interface is less distinct and the suspended particles settle individually. The transition from these collective to individual motions of suspended particles is controlled by the border resolution of concentration interface. We define the dimensionless parameter which describes the border resolution of concentration interface by the ratio of average particle distance  $d_p/\phi^{1/3}$  ( $d_p$ : particle diameter,  $\phi$ : concentration) to the dominant wavelength of the instability  $\lambda$ . As can be seen in Figure, the dimensionless parameter well describes the transition from fluid-like to particle-like behaviors. The suspended particles (and the interstitial fluid) perfectly behaves as continuum for  $d_p/\phi^{1/3}\lambda < 0.03$  and behaves individually relative to fluid for  $d_p/\phi^{1/3}\lambda > 0.2$  [5].

The similar collective motion of suspended particles has been studied on the settling of particle clouds in viscous fluid. Some researchers have suggested that the collective motion of particles in clouds can be explained by the swarm of Stokeslet [7]. They have found that the particle cloud behaves collectively when the flow generated by each particle (Stokeslet) enough screens the surrounding flow. If the above parameter is rewritten by number density of particles  $N$ , it is expressed as  $(6/\pi)^{1/3}/N^{1/3}\lambda$ . Therefore the border resolution of concentration interface express the discretization of space by Stokeslet  $1/N^{1/3}$  for a given lengthscale  $\lambda$ .

One more interesting similarity to previous study is the wavelength of instability. From the linear stability analysis of Rayleigh-Taylor instability on both miscible and immiscible interfaces of pure fluids [8], it is found that the dominant wavelength of miscible interface with no diffusion and immiscible interfaces with no interfacial tension are asymptotically close to constant value. The wavelength at concentration interface is also close to the asymptotic value [9]. From this point of view, the concentration interface can be interpreted both as the the immiscible interface with no interfacial tension and the miscible interface with no diffusion.

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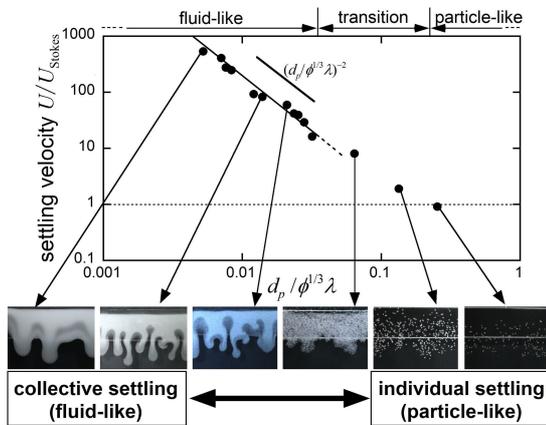


Figure 1: Collective and individual settlings of suspended particles in Hele-Shaw cell.

## Reverse chemical garden reaction of cementitious materials

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Recent advances in the nano-scale mineralogy extend from the extraterrestrial materials known as in cosmic dusts and asteroids to ordinary industrial materials like the cementitious materials. The distinct property of nano materials can be characterized from the points of view of (1) nucleation, (2) self-assembly behavior and (3) flexibility in the form.

A very common industrial material, cement is a typical one consisted of nano particles of calcium silicate hydrates (C-S-H).

Crystal growth experiment of cementitious materials can be recently performed using interferometric and nanoscopic techniques. Although the cement reaction producing C-S-H from silicates with  $\text{Ca}(\text{OH})_2$  (portlandite: CH) or more alkaline solution is extensively occurring at buildings under and after construction, similar reaction is expected at the interface of natural rock and concrete-building such like tunnel, dam and underground repository for radioactive wastes.

Hyper alkaline alteration experiment using vertical scanning interferometer revealed the precipitation behavior of C-S-H by reverse chemical garden reaction on natural rock (Satoh et al., in press). Very slow growth rate of the C-S-H on rock was observed to be  $\sim 2.4\text{E-}3$  nm/s. The ionic selection of the solutes through the C-S-H wall having nanopores like membrane was also confirmed.

Most recently, we applied newly developed ultramicroscopic technique with fluid reaction TEM (FR-TEM: Poseidon) for study of reverse chemical garden reaction between silica fume (Elkem Microsilica 940-U,  $\sim 150$  nm) and CH-saturated solution. It revealed that the reaction caused silica hydration (volume expands) and subsequently form string and veil of C-S-H. The growth rate of string C-S-H was calculated to be  $\sim 4.5\text{E-}2$  nm/s, which is fast enough to form frame network preparing veil-formation. It was chemically confirmed by FESEM-EDS that this C-S-H veil evolved toward Ca-rich over time. Our observed result could be a fundamental process of reverse chemical garden reaction, i.e., cement-solidification.

Ultramicroscopic investigation of C-S-H growths may improve the simulation of groundwater conditions in the future.

Keywords: reverse chemical garden reaction, cementitious material, C-S-H, fluid reaction TEM

## General nature of liquid-liquid transition in aqueous organic solutions

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Contrary to the conventional wisdom that there exists only one unique liquid state for any material, there are growing experimental and numerical pieces of evidence for the existence of more than two liquid states in a single component substance. The transition between them is called liquid-liquid transition (LLT). LLT has attracted considerable attention because of its importance in the fundamental understanding of the liquid state. However, the physical nature of the transition has remained elusive. Particularly for water, the possible existence of LLT has special implications not only on its fundamental understanding, but also on a link of various thermodynamic and transport anomalies with critical anomaly associated with LLT. Here we reveal that 14 aqueous solutions of sugar and polyol molecules, which have an ability to form hydrogen bonding with water molecules, exhibit liquid-liquid transitions. We find evidence that both melting of ices and liquid-liquid transitions in all these aqueous solutions are controlled solely by water activity, which is related to the difference in the chemical potential between an aqueous solution and pure water at the same temperature and pressure. Our theory shows that water activity is determined by the degree of local tetrahedral ordering, indicating that both phenomena are driven by structural ordering towards ice-like local structures. This has a significant implication on our understanding of the low-temperature behaviour of water.

Keywords: liquid-liquid transition, water and aqueous solution, supercooled liquids and glasses

## Direct Observation of Crystallization Process in a Solution using Transmission Electron Microscopy

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Nucleation is a fundamental event that determines the size, number and morphology of produced crystals. Therefore, the nucleation process must be clarified to form products efficiently and to predict mineralization in various environments. The direct approach to understanding nucleation would be atomic-scale in-situ observation, for which a transmission electron microscope (TEM) would be a most powerful tool. However, the experimental conditions for TEM are limited, and there have been only a few reports on the in-situ observation of nucleation processes to date. In particular, since TEM needs a high vacuum, crystallization experiments in a solution are generally impossible. Recently, the processes of formation of nanoparticles and coalescence in a solution were finally observed using specially designed cells in a TEM [1-3]. However, live observation of the dynamics of the earliest stages of nucleation - those taking place before the formation of a stable crystal - had never been achieved before our recent work [4]. We overcame the difficulty by using an ionic liquid, which has negligible vapor pressure and is not charged up by the electron beam due to its relatively high electron conductivity, and by aiming to visualize the dynamics of nucleation under conditions very close to equilibrium, where the nucleation rate must be small but the conditions for TEM observation are more stable. We used two TEMs at an acceleration voltage of 200 kV (Hitachi H-8100, installed at Tohoku University, Japan) for the nucleation experiment and 300 kV (Hitachi H-9500, installed at Hitachi High-Technologies Corporation, Ibaraki, Japan) for the in-situ heating experiment.

An ionic solution could be observed stably under normal electron irradiation conditions as expected. Nucleation of sodium chlorate crystals was directly observed in the TEM at room temperature. Then, the sample was heated up in the TEM. The main results of the heating experiment were as follows:

1. Nanocrystals were not only dissolved but also newly formed even in the totally dissolving system, i.e., probably an under-saturated condition.
2. Both stable and metastable crystals nucleated independently of their respective solubility. However, metastable crystals were dissolved in a shorter residence time.
3. The total number of smaller particles decreased with the formation of new particles by the Ostwald ripening at or near equilibrium conditions.
4. High-density fluctuations may lead to nucleation even under equilibrium conditions.

We describe the ongoing results to elucidate the dynamics of nucleation at the nanoscale, as well as the growth, coalescence and dissolution of nanocrystals in a solution.

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Keywords: Nucleation, In-situ observation, TEM, Ionic liquid

## Emergence and Amplification of Chirality via Achiral-Chiral Polymorphic Transition in Sodium Chlorate Solution Growth

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Chirality is the concept that widely spreads in nature at various levels from elementary particles to morphology of plants. Although both the enantiomers have equal stability, lives on the earth preferentially selects one-type of the two enantiomers. This phenomenon is called homochirality, and its origin (the emergence of chirality) and the amplification of chirality are great puzzles in the evolution of life on the primitive earth. One candidate of the origin includes chiral crystallization of achiral compounds. Sodium chlorate ( $\text{NaClO}_3$ ) undertakes chiral crystallization from achiral solution.  $\text{NaClO}_3$  has chirality in its crystal structure due to the enantiomorphic space group of  $P2_13$  (cubic). A *static* solution of the compound yields statistically equal numbers of the two enantiomorphs. However, Kondepudi *et al.* have strikingly revealed that a *stirred* solution yields only one-type of the enantiomorphs[1]. The mechanism of the significant chiral bias has not been elucidated. Diverse crystallization experiments have implied that the emergence and the amplification proceed during the early stage of crystallization. However, a direct investigation of the early stage is still missing. We therefore have carried out in-situ observations focusing on the early stage. The observations have revealed that achiral metastable crystals having  $P2_1/a$  symmetry (monoclinic) appear prior to the formation of chiral crystals. The authors have reported this result in JpGU 2011[2]. Here, we present more detailed observations, and demonstrate that polymorphic transformation from the achiral phase to the chiral phase can be responsible for the emergence and the amplification.

A droplet (6  $\mu\text{l}$ ) of  $\text{NaClO}_3$  aqueous solution saturated at 22 °C was put on a glass slide whose temperature is controlled at 22 °C by a Peltier device, allowing the droplet to evaporate isothermally. We observed crystallization process induced by the evaporation using a polarized light microscope. The microscope enables us to distinguish cubic crystals from non-cubic crystal by detecting birefringence, allowing us to distinguish chiral crystals from achiral crystals, and it can identify handedness of the chiral crystals by detecting optical rotation.

Polymorphic transformation from an achiral crystal to a chiral crystal was observed. The transformation could be classified into two kinds according to their transition rate. The slower one proceeds at 35  $\mu\text{m}/\text{sec}$  (Fig.A), and the faster did at 2000  $\mu\text{m}/\text{sec}$  (Fig.B). The slower transformation was induced by a contact with a chiral crystal. It is noteworthy that the resulting enantiomorph generated through the contact-induced transformation was certainly the same as the enantiomorph that contacted with the achiral crystal. The double digit difference in a rate of the two transformations is probably ascribed to difference in the mechanism, indicating the slower transformation and the fast one are solvent-mediated phase transformation (SMPT) and structural phase transition (SPT), respectively. The SPT probably generates both the enantiomorphs in equal probability since the activation energy required to transform should be equal. In contrast, the contact-induced SMPT preferentially generates the same enantiomorph as the contacted crystal. This inheritance of chirality through the contact-induced SMPT is possibly responsible for the amplification of chirality.

So far, the emergence and the amplification have been explained by primary nucleation of a chiral crystal and secondary nucleation from the crystal. In contrast, our observation provided a new sight based on the achiral-chiral polymorphic transformation: the emergence of chirality through the SPT and its amplification through the contact-induced SMPT.

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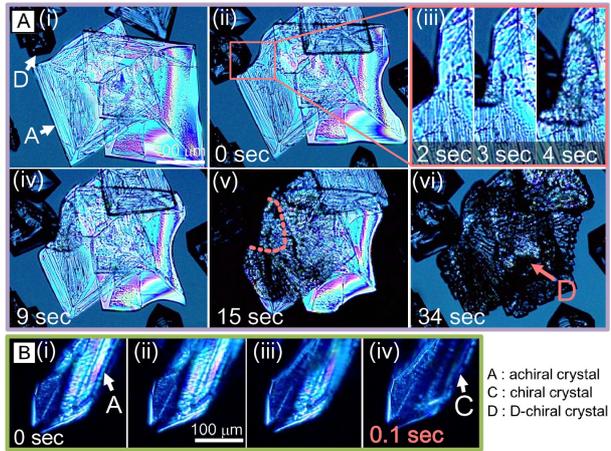
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Keywords: sodium chlorate, chiral symmetry breaking, chiral crystallization, metastable phase, polymorphic transformation, in-situ observation

MIS36-05

Room:314

Time:May 1 11:45-12:00



## Theoretical analysis on the stability of divalent cations in the surface sites and clusters of calcium carbonate

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Formation process of calcium carbonate polymorphs, calcite, aragonite and vaterite has been extensively investigated, and impurity effect has been proposed as controlling phenomena in order to account for the formation of a particular polymorph. For example, it has been reported that an addition of  $Mg^{2+}$  in a solution inhibits calcite formation and promotes aragonite formation, however incorporation mechanism of this kind of impurities is poorly understood.

In general, smaller divalent cations than  $Ca^{2+}$ , like  $Mg^{2+}$ , cannot form solid solution with aragonite. However, the structure of a crystal surface or small cluster forming at an initial stage of crystal growth can be different from the bulk crystal because of its flexibility, and it can act as the site for incorporation of ions which is unstable in the bulk structure. In the present study, the stability of divalent cations, especially  $Mg^{2+}$ , (1) on hydrated aragonite surface and (2) in the cluster forming in an early stage of nucleation was investigated by quantum-chemical calculations, and the impurity effects on the formation of polymorphs were discussed.

The calculation results show that  $Mg^{2+}$  is easier to be incorporated into a small cluster, while the hydration energy of  $Mg^{2+}$  is higher than that of other divalent cations. This indicates that  $Mg^{2+}$  is difficult to be released from hydration shell, however, once released, it is easy to incorporate into the cluster. Atomic arrangement of these clusters including  $Mg^{2+}$  is different from that of additive-free  $CaCO_3$  clusters. Furthermore,  $Mg^{2+}$  on the aragonite surface considerably affects the surface structure and has an influence on the stability of aragonite. Thus, incorporation of  $Mg^{2+}$  into the clusters and surfaces sites should play an important role on the formation of the crystalline nuclei and the consequent crystal growth.

Keywords: calcium carbonate, impurity, crystal growth

## Atomic scale in situ observation of solid-liquid interface of calcite

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Calcium carbonate is one of common minerals on the earth. Calcium carbonate crystals are utilized industrially in various fields, so that the control of crystal growth is required. It has been known that organisms control the morphology and polymorph of calcium carbonate crystals by utilizing inorganic and organic additives in biomineralization. Understanding the additive effects on growth of calcium carbonate crystal is necessary to control the crystal growth.

The effect of additives on growth of calcite which is a stable polymorph of calcium carbonate has been investigated. The additive effect on calcite surface, such as incorporation of magnesium ions into calcite and pinning of step propagation by organic molecules has been confirmed. On the other hand, the additive effect on hydration of calcite has remained unclear even if that effect has been suggested by the measurement of growth rate of calcite in the presence of additives. Hydration affects adsorption and surface diffusion of ions on calcite surface. Also, the dehydration has been considered as rate-determining process in solution growth by the estimation of energy barriers of solution growth processes. Therefore, hydration is a key to control the kinetics of calcite growth.

Hydration at the vicinity of calcite surface has been measured by surface X-ray diffraction. Although this technique made the description of hydration structure clear, it does not show the local difference of hydration structure between on the terrace and the step front which is capture site of ions. Hence, we employed the newly frequency modulation atomic force microscopy (FM-AFM) for in situ observation of local hydration structure in atomic scale. This technique is expected to provide insight into the atomic scale distribution of hydrated water molecules in growth solution even at step front. This study describes the first in situ examination of the additive effect of organic molecules and magnesium ions on local hydration structure of calcite surface in atomic scale utilizing FM-AFM. The hydration images were compared with the growth rate of calcite measured using phase shift interferometry so as to validate the influence of hydration on the growth rate of calcite.

The findings are summarized as follows:

- (1) The synthetic polypeptide, even that with high hydrophilicity, does not affect hydration at the surface of calcite.
- (2) Combination of magnesium ions and the synthetic polypeptides provides a rigid hydration on calcite surface.
- (3) Magnesium ions and the synthetic polypeptides influence hydration and the surface pattern of calcite, respectively.
- (4) Structured water distribution eases the energy gap between the calcite surface and solution. As a result, the interfacial tension between the calcite surface and the solution is decreased.
- (5) Magnesium ions and the synthetic polypeptide act in unison to accelerate nucleation via changes in hydration structure.
- (6) Hydration contributes to interfacial energy between the calcite and the solution, but not for the adsorption of ions on the calcite steps.

This study demonstrated that additives affect the interfacial tension via altering hydration structure by application of FM-AFM for crystal growth experiment for the first time. Our results also showed that there is hardly any change in the adsorption of ions on calcite surface due to the hydration structure. That suggests that dehydration is not a rate-determining process, an observation that is contrary to the currently prevailing theory. The further observation of hydration of step front will be carried out by FM-AFM to demonstrate the effect of hydration on adsorption of ions. These findings indicate that the control of interfacial tension is possible utilizing the additive effect on hydration. That provides a new knowledge to regulate the polymorphism of calcium carbonate.

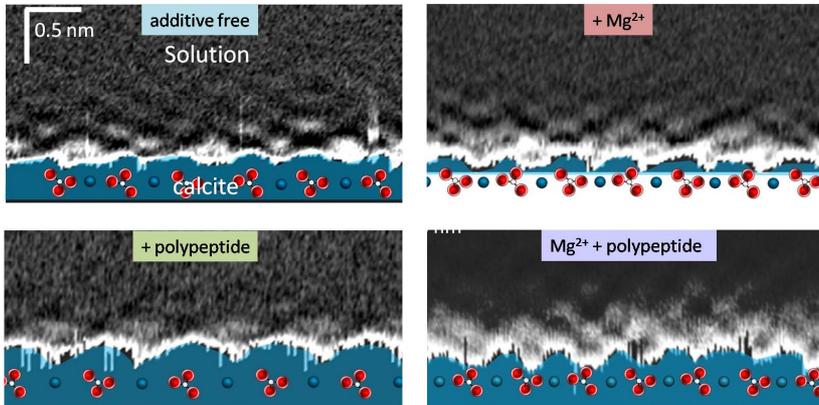
Keywords: Calcite, Hydration, FM-AFM

MIS36-07

Room:314

Time:May 1 12:15-12:30

FM-AFM images of Hydration structure on calcite



## Impurity partitioning in colloidal crystallization

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Colloidal crystals are regarded as a promising tool to investigate diverse basic physical phenomena. We have applied this colloidal crystal to impurity partitioning in the melt growth. Since no research has been focused to detail partitioning behavior of colloidal crystals, the objective of the present work is to reveal a partitioning behavior during colloidal crystallization.

A few amount of impurities (2 percent) were doped to the colloidal dispersion, from which colloidal crystals were grown with convective assembly method. Polystyrene particles (PS) were used for fabricating colloidal crystals, and different sizes of PS and fluorescent bearing PS (w/fluor.) were doped as impurity particles.

In each particle size for two kinds of impurity, effective partition coefficient ( $k_{eff}$ ) were measured at various growth rates. Obtained  $k_{eff}$  gives  $k_0$  by using BPS plot. The  $k_0$  is decreased as the difference between the size of the impurity and the 500 nm host particle increased. The  $k_0$  of each w/fluor. was larger than that of the corresponding pure PS. Moreover, the value of  $k_0$  for the 520 nm w/fluor. surpassed unity, whereas the PS is always less than unity.

We have employed a Thurmond and Struthers (T&S) model (J. Phys. Chem. 57, 831 (1953)) to discuss the difference of  $k_0$  for PS and w/fluor. particles. T&S model shows  $k_0$  as;  $k_0 = \exp((\Delta G_{Tr} - \Delta H)/RT)$ . Here,  $\Delta G_{Tr}$  is free energy difference between the solid and liquid phases of an impurity at the transition temperature, T,  $\Delta H$  is the excess enthalpy which is caused by incorporation of the impurity into the host material, and R is a gas constant. We have determined the phase transition volume fraction for PS and w/fluor. to evaluate the  $\Delta G_{Tr}$ . It was shown that  $\Delta G_{Tr}$  of w/fluor. is positive whereas PS is zero. This leads to larger  $\Delta G_{Tr} - \Delta H$  of w/fluor. than that of PS, which corresponds to larger  $k_0$  of w/fluor., and in a small  $-\Delta H$  range,  $k_0$  of w/fluor. surpasses unity. We have found the difference of  $k_0$  for different kinds of impurity particles, and succeeded in applying concept of T&S model to partitioning of colloidal crystals.

Keywords: Colloidal crystal, Impurity partitioning

## Mechanism of ice nucleation on (100) plane of calcium oxalate monohydrate: a molecular dynamics simulation study

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Calcium oxalate monohydrate (COM) is the most thermodynamically stable polymorph of calcium oxalate. COM is known as an organic mineral formed on the surface of the Earth, under the bottom of sea, in atmosphere, in meteorites, in plants and in kidney stones. So far, COM has been studied in fields of mineralogy, biology and medical science.

Recently, Ishikawa et al. suggested that COM plays as an ice nucleation promoter, like silver iodide and ice nucleation-active bacteria. They speculated that the structure of COM (100) plane induces ice nucleation. Studies on the mechanism of ice nucleation promotion by COM are important, because the studies may help provide development of new materials to make artificial snow. Molecular dynamics (MD) simulation is a helpful method to investigate the mechanism of ice nucleation at the molecular scale. Thus, we performed a MD simulation to elucidate the mechanism of ice nucleation on the (100) plane of COM.

In the simulation, the intermolecular interaction between a pair of water molecules was estimated using a six-site model. The water-COM interaction was estimated using a COM potential model proposed by Tommaso et al. In the <100>direction of COM, two different molecular layers are piled up by turns; one is positively-charged Ox-1 layer consisting of calcium ions and oxalate ions, and the other is negatively-charged Ox-2 layer consisting of oxalate ions and water molecules. In this study, the simulation was performed for a rectangular parallelepiped system in which supercooled water consisting of 4000 water molecules was sandwiched by Ox-1 and Ox-2 layers. Temperature was set to 268 K. Total run was 4 ns or longer. The simulation indicated the formation of a polar cubic ice structure near the Ox-2 layer. However, the formation of a hexagonal ice structure was not observed. Details of the simulation results will be shown at the presentation.

This work was supported by a Grant-in-Aid for Scientific Research (No. 22107004) on Innovative Areas of "Fusion Materials (Area No. 2206)" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Keywords: crystal growth, nucleation, ice, organic mineral, computer simulation, calcium oxalate

## Observation of admolecule on the crystal surface in liquid by non-contact atomic force microscopy

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The highest resolution AFM images are obtained by non-contact atomic force microscopy (NC-AFM). Fukuma et al. (2005) succeeded in obtaining true atomic resolution images by NC-AFM in spite of the liquid environment [1]. We are interested in the crystal growth process. However, previous NC-AFM studies were only about insoluble crystals in liquid. NC-AFM is not good at investigating the moving surface because NC-AFM is a very sensitive method for detecting weak interaction force. Therefore, we tried to observe several soluble crystals in liquid by NC-AFM at first.

At first, we observed tetragonal lysozyme (110) face in saturated solution by using homebuilt Non-Contact AFM (NC-AFM). We could observe individual molecules on the lysozyme (110) face in liquid for the first time and determine the crystallographic position of each molecule [2]. In addition, we also observed admolecule and point defect on the lysozyme surface in liquid.

### Acknowledgments

We thank Prof. S. Morita of Osaka University, M. Abe of Nagoya University, and Shimadzu Corporation for observation of AFM.

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Keywords: AFM, Crystal growth, Atomic resolution image, Admolecule, Protein crystal

## In-Situ Observation of Protein Crystal Growth in The International Space Station

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In-situ observation of protein crystal growth was conducted at the international space station in 2012. Both growth rate and surface topography of lysozyme crystals vs supersaturation and purity of the solution were measured for the first time by interferometry in space. The differences from ground-based experiments became clear to answer the question "Why better crystal could be grown in space?".

Keywords: crystal growth, space experiment, microgravity

## In situ simultaneous SEM/STEM observation of Pt/C catalysts in a gaseous atmosphere

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In order to gain fundamental understanding of the degradation mechanisms of Pt/C catalyst, there is an increasing demand on the nanostructural characterization using TEM. We have developed the humid-air supply system in TEM, H-9500 300 kV TEM and we have success the deterioration mechanism of fuel cell electrocatalyst<sup>1</sup>. Recently, we developed in situ simultaneous SEM/STEM observation technique for surface analysis of catalyst materials using a HF-3300 Cold-FE TEM with SEM/STEM function. We succeeded in visualizing of three-dimensional movement of the Pt particles on the carbon support in the gas atmosphere by this observation technique.

In situ simultaneous SEM/STEM observation of the platinum catalysts on carbon support (Pt/C; Pt: 29 wt.%) in the air conditions were carried out using HF-3300 equipped with the Cold-FE gun and the SEM/STEM function. A gas injection-heating specimen holder<sup>2</sup> was used for the Pt/C powder heating and gas injection. Pt/C powder mounted on the tungsten wire was heated to 200 deg C in a TEM, and then, while air was spraying (up to  $1.2 \times 10^{-2}$  Pa) from the injection nozzle to the Pt/C, the behavior of the Pt/C was recorded as the movie file. After the air injection at about  $1.0 \times 10^{-3}$  Pa, the coalescence growth between Pt particles on the carbon support was observed, and the Pt particles gradually started inserting into the carbon support. After that, most all of the Pt particles on the carbon support disappeared from the surface of the carbon support. And the carbon support structure was changing into a porous morphology.

We can observe that the behavior of the Pt particles on the carbon support was penetrated into the carbon support by in situ simultaneous SEM/STEM observation. These results demonstrate that the penetration of Pt particles to carbon support affects the degradation mechanism of a Pt/C electrocatalyst.

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Keywords: electron microscope, in situ observation

## Low temperature crystallization of free-flying silicate nanoparticles investigated by in-situ IR measurement experiment

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Dust is typically 100 nm sized nanoparticles which can be observed ubiquitously in the universe. Dust forms from the high temperature gas in the out flow of evolved stars and dispersed into interstellar space. Silicate dust is one of the most abundant minerals in the universe including, shells around evolved stars [1], disks around young stars [2], comets [3] and so on. So its formation mechanism is the key process to understand the lifecycle of dust. Especially, 10  $\mu\text{m}$  IR band structure from 8  $\mu\text{m}$  to 12.5  $\mu\text{m}$  in wavelength arising from Si-O stretching provides us mineralogical character of silicate. The Infrared Space Observatory mission revealed the existence of crystalline silicates around evolved stars based on the 10  $\mu\text{m}$  band feature mainly attributed to amorphous silicate [4]. Numerous laboratory experiments to reproduce the observed spectra such as direct condensation [e.g. 5] and annealing of amorphous silicates [e.g. 6] showed variation in the IR spectra due to structure, chemical composition, temperature, size and shape, and proposed formation mechanisms of crystalline silicates. Nevertheless the scenario is not fully understood. One of the most important discrepancies concerning the dust formation process is a detection of an IR feature attributed to crystalline silicates at low temperature region, typically <300 K [1] in contrast to amorphous silicates at high temperature region [4]. Low temperature crystalline silicates cannot be explained by direct condensation or annealing involving high temperature process.

Recently, we have investigated new IR measurement technique for free-flying nanoparticles which enabled direct comparison with astronomical observation without KBr medium effects which pervert its band structure such as peak wavelength, FWHM and relative intensity [7]. Applying the new IR technique, we investigated condensation of Mg-bearing silicate from thermally evaporated magnesium and silicon oxide under the atmosphere of O<sub>2</sub> and Ar based on 10  $\mu\text{m}$  band.

*In-situ* IR measurement revealed initial condensates were amorphous or droplet of Mg-bearing silicate and its crystallization took place at <500 K. Furthermore, crystallization kept proceeding through lower temperature region. Produced particles showed core-mantle like structure, amorphous silica covered with polycrystalline forsterite observed by Transmission Electron Microscope.

Prevailing annealing experiments reported that 1000 K is required for crystallization of forsterite [8]. This critical discrepancy may be explained by nano size effects. When immoderately small particle nucleates, a particle takes metastable amorphous or droplet phase because of lower melting point of a nanoparticle [9] and larger diffusion coefficient of molecules in a nanoparticle distinct from in bulk [10]. In case the condensates were droplet due to the size effects, activation energy of crystallization is significantly low compared to amorphous [11]. We concluded such characteristic phenomena in nanometer scale enabled low temperature crystallization in the same way as the circumstellar environments.

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Keywords: astromineralogy, nanoparticle, experiment, IR

## Free energy of cluster formation and a new scaling relation for the nucleation rate

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Recently we performed molecular dynamics (MD) simulations of homogeneous nucleation from vapor for systems of  $(1-8) \times 10^9$  Lennard-Jones atoms [Diemand et al. J. Chem. Phys. 139, 074309 (2013)]. The very large MD simulations allow us to determine the formation free energy of clusters accurately over a wide range of cluster sizes, for the first time. This is now possible because such large simulations allow for very precise measurements of the cluster size distribution in the steady state nucleation regime. The peaks of the free energy curves give critical cluster sizes, which agree well with independent estimates based on the nucleation theorem. Using these results, we derive an analytical formula and a new scaling relation for nucleation rates:  $\ln J' / \eta$  is scaled by  $\ln S / \eta$ , where the supersaturation ratio is  $S$ ,  $\eta$  is the dimensionless surface energy, and  $J'$  is a dimensionless nucleation rate. This relation can be derived using the free energy of cluster formation at equilibrium which corresponds to the surface energy required to form the vapor-liquid interface. At low temperatures (below the triple point), we find that the surface energy divided by that of the classical nucleation theory does not depend on temperature, which leads to the scaling relation and implies a constant, positive Tolman length equal to half of the mean inter-particle separation in the liquid phase.

Keywords: nucleation, molecular dynamics simulation, nucleation rate, scaling, free energy of cluster formation

## High-speed polarized in-situ observation in a nucleation process of nanoparticles produced by the gas evaporation method

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The gas evaporation method has been investigated for more than half a century since the Kubo effect was reported (1962). There have been many studies on the produced nanoparticles mainly using a transmission electron microscope, which have elucidated the different physical properties of nanoparticles from those in bulk. On the other hand, there have been almost no reports on nucleation in smoke related to crystal growth. Recently, we achieved in-situ observation of the nucleation process in smoke using a double-wavelength Mach-Zehnder-type interferometer, which can determine the temperature and pressure at the nucleation simultaneously. A series of experiments clearly showed that smoke particles condense homogeneously only in a very high supersaturated environment [1-3]. In a preliminary experiment using tungsten trioxide, the smoke particles condensed with a degree of supersaturation as high as  $\sim 10^6$ . In this process, since evaporant is continuously supplied into the surrounding of the evaporation source, the flow of smoke after the nucleation and growth of nanoparticles has been simply considered as a consecutive process. The nucleation and growth of smoke particles should be a rapid process (ms order) due to high supersaturation, so the concentration of the evaporated vapor drastically decreases. However, the details of the formation process remain unknown.

In this study, we attempted to visualize the nucleation of nanoparticles and motion of smoke using a high-speed polarization image sensor (Photron Inc.) to clarify the details of the nucleation process of smoke particles. Since the sensor itself has pixels with micro-polarizers, a phase shift interferogram can be obtained in less than a millisecond because of the lack of mechanical movement free, and can therefore be applied to rapid phenomena such as nucleation in vapor phase. Here, we show the preliminary results of homogeneous nucleation of tungsten oxide from vapor phase.

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[2] Y. Kimura, K. Tsukamoto, Interferometric observation of temperature distributions in the smoke experiment, *J. Jpn. Soc. Microgravity*, 28 (2011) S9-S12.

[3] Y. Kimura, K. K. Tanaka, H. Miura, K. Tsukamoto, Direct observation of the homogeneous nucleation of manganese in the vapor phase and determination of surface free energy and sticking coefficient, *Crystal Growth & Design*, 12 (2012) 3278-3284.

Keywords: Nucleation, High-speed polarized camera, in-situ observation

## In-situ observation of nucleation process of calcium carbonate by the fluid-reaction TEM

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Recent studies have reported achievements of in-situ observation of the nucleation and crystallization studies using transmission electron microscope (TEM), and several new perspectives for non-classical pathway of crystallization [1-4]. Calcium carbonate generates a lot of attention because of complex nucleation due to appearance of various polymorphs in addition to availability for industrial materials such as paper and paint, and reservoir of carbon dioxide, and biomineralization. We also focus on the calcium carbonate in view of selection of polymorph in nucleation process. In case of nucleation from relatively higher supersaturated solution, nucleation of amorphous phase prior to crystalline phase has been known [5,6]. Kawano et al. have been reported an in-situ observation of solution-mediated phase transition from amorphous phase into crystalline phase under optical microscope [6]. The Ostwald law of stages has been believed to occur in many cases. Contribution of prenucleation cluster, which was confirmed by using the cryo-TEM [8], to the nucleation has also been reported [7]. However the generality or solution condition to take these processes is still not obvious.

Now, we have performed energetically a project to observe crystallization and dissolution processes in an aqueous solution using ionic liquid instead of water or the "Poseidon" (Protochips Inc.), which is a sample holder having a liquid cell for TEM observation. We call our TEM fluid-reaction TEM (FR-TEM), which is able to perform crystallization experiments in a solution including both methods. Here, we have been tried to observe whole the process of crystallization of calcium carbonate via amorphous phase using fluid-reaction TEM and actually observed a solid-state phase transition from amorphous phase into a crystalline phase by in-situ observation.

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Keywords: Fluid-reaction TEM, In-situ observation, Calcium carbonate, Nucleation

## In-situ TEM observation of dissolution processes in aqueous solutions using "Poseidon"

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Recently, we started a new project to observe crystallization and dissolution processes of crystals in a solution using two different methods under transmission electron microscope (TEM). To overcome the difficulties to introduce a solution into a TEM, Kimura et al. used ionic liquid to avoid evaporation of a solvent in the high-vacuum of a TEM [1]. As the result, several new insights were found: solubility-independent formation of polymorph; crystals do not dissolve smoothly but in a fluctuating manner; and new crystals form even in a totally dissolving system. Another advantage of this method is that the growing crystal does not have a hydrated layer on their surface. It has been believed that dehydration process has a largest potential barrier to incorporate a unit cell into the crystal. However, no one ever visualized the process and it has been totally veiled. The water free experiment using an ionic liquid may give us a new perspective on the dehydration process by comparison with experiments in general aqueous solutions. Now, we are forwarding a project to observe crystallization and dissolution processes in an aqueous solution in atomic-scale using the "Poseidon", which is a sample holder having a liquid cell for TEM observation. We call our TEM fluid-reaction TEM (FR-TEM) including both solution growth experiments using an ionic liquid and the Poseidon.

Poseidon (Protochips Inc.) give us the opportunity to visualize the three-dimensional process with several advantages compared with previous works using an atomic force microscope, which is able to observe only two-dimensional, and an optical microscope, which has much less lateral resolution. Growth and dissolution processes at the first top layer (surface) of a crystal have been energetically studied long time using these tools. However, the detail process in atomic scale has been observed very limited. Therefore, the aims of our project is understanding of three dimensional nucleation including Ostwald law of stages based on phase determination by electron diffraction, determination of very slow dissolution rates, and dissolution process in terms of an influence of defects. Here, we will show the first pictures about the movements of nanoparticles and dissolution of amorphous silica and crystalline silicate samples.

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Keywords: Fluid-reaction TEM, Dissolution, In-situ observation

## Mineral size distribution modeling during dissolution of montmorillonite

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In the geological disposal of radioactive waste, the waste is sealed by cement-based materials and bentonite-based material to prevent leakage into environment. The bentonite-based material protect the radioactive waste from the groundwater flow around the geological disposal area, so its low permeability should be maintained for a long term. The low permeability could be achieved by the swelling of montmorillonite in the bentonite-based material. However, montmorillonite will dissolve by a reaction with high-alkaline pore water, spoiling the low permeability of the bentonite-based material. In addition, precipitation of secondary minerals such as zeolite will promote the dissolution of montmorillonite through changes in composition of the pore water. In order to assess the long-term permeability of the bentonite-based material, it is necessary that the dissolution of montmorillonite and crystallization of secondary minerals are comprehended over a long time of several tens of thousands years.

In the pore water, there are numerous montmorillonite particles of various sizes. When montmorillonite of various sizes co-exists in the same solution, the smaller particle dissolves faster than the larger one because of the Thomson-Gibbs effect. The mean size of montmorillonite will increase gradually, leading to a delay of further dissolution. In addition, an evolution of size distribution is also important for the crystallization process of the secondary minerals, e.g., zeolite. Since zeolite is not present in the initial solution, the crystallization process is described in the nucleation and subsequent growth. Evolution of the size distribution of zeolite affects the dissolution of montmorillonite through changes in solution composition. This implies that the evolution of the size distribution of montmorillonite and zeolite should be considered to assess the long-term behavior of the permeability of the bentonite-based materials. However, in the previous chemical equilibrium calculations, the evolution of the size distribution has not been considered.

In this report, we numerically modeled the time evolution of the size distribution of montmorillonite due to dissolution according to a theoretical model described in Yao et al. (1993). The crystallization of zeolite was neglected as a first step. We consider the dissolution of montmorillonite in a closed system. The evolutions of the size distribution, bulk concentration of solution, and mean radius of montmorillonite were successfully calculated.

The model given in this report is a model in a closed system. On the other hand, the geological disposal environment is not a closed system because there is an actual mass transfer due to the flow of groundwater and diffusion. To couple the local mineral dissolution/crystallization and the global mass transfer, some chemical reaction-mass transfer calculation codes have been developed. However, these codes assumed chemical equilibrium, so the evolution of the size distribution of minerals did not considered. The evolution of the size distribution of minerals would significantly affect the long-term behavior of the permeability of the bentonite-based materials. Therefore, it is important to compare the calculation results of the model with the evolution of the size distribution and chemical equilibrium calculation result.

Keywords: montmorillonite, dissolution, Mineral size distribution

## Advanced techniques in the latest quantitative image analysis for crystal growth experiments

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In the research field of crystal growth science, the targeted scales are varied from nano-scaled small space to visible large space. Recently the spatial scale expands toward underground or orbital space. In the metrology field, there is the scaling-law for xyz-t space-time space, beyond which we extend the measurable limits.

The contactless microscopes like interferometers or laser microscopes are very valuable tools for analyzing crystal growth in long time and surface-features in wide area because they have advantages to obtain data in high speed without spoiling the sample surface. Their time-scale is variable in the off-line processing, if the data were sequentially obtained by auto-measurements, so that we can trace the real growth phenomena. By this method, we succeeded to observed lysozyme growths in the International Space Station laboratory, ice-water interface and dissolving clay.

Moreover, the spatial scale can be changed by shifting the field of view with observing and the off-line process of these obtained images as stitching. In general, huge data fragments measured by certain time interval or position shifting contain offsets or distortions and the data amount is much bigger than the speed of manual corrections. Hence, there are many cases that whole data cannot be utilized for final analysis. We attempted to eliminate artifacts generated by microscopes using a system consist of commercially supplied software and dedicated plug-in programs for consistent normalizations and corrections between planes to be stitched.

In this session, we will introduce some examples tried quantitative analysis of huge multiple data including the time-line display expressing time-based changes at certain line on a plane of growing and dissolving crystal surfaces.

Keywords: image analysis, time-space scale, topography, huge stitching

## IP6 as a silver carrier agent and formation of Ag nanostructures

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In recent years, people have become aware of the importance of natural organic materials in geological systems. It would be important to clarify the interaction between natural organic materials and metallic ions.

Phytic acid, known as inositol hexakisphosphate (IP6), or phytate, C<sub>6</sub>H<sub>18</sub>O<sub>24</sub>P<sub>6</sub>, is found within the hulls of nuts, seeds, and grains, and it is the principal storage form of phosphorus in many plant tissues, especially bran and seeds. IP6 is not digestible to humans and animals, and phytic acid chelates make unabsorbable certain important minerals such as zinc, iron, calcium and magnesium.

On the other hand, for many years, it has been known that silver works for its catalytic activities, anti-microbial activities, and used to avoid infections and prevent spoilage. Many researchers have focused on the anti-bacterial, ability to kill microorganisms and multi-functional properties of silver nano-particles.

In this study, it is demonstrated that IP6 plays a role as a metal carrier agent for the formation of metallic nanostructures. For the preparation of the IP6 with Ag elements (Ag-IP6), The commercial IP6 solution (50 %) was diluted with distilled H<sub>2</sub>O at the H<sub>2</sub>O:IP6 solution ratio of 9:1, then 1g of AgNO<sub>3</sub> was added to the diluted IP6 solution of 100 ml, and long-term stabilized small Ag clusters were formed in the solution. A drop of the solution was dripped onto metallic substrates, then kept for the treatment time of 10 s to several min at room temperature. The solution was immediately dried using a gas burner or hot plate. Then, the reaction of the Ag-IP6 with several kinds of metals was examined. The structural and morphological properties of the Ag nanostructures were characterized by scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with EDS. In addition, the surface condition of the Ag nanostructures reacted with Cu or Al and dried IP6 complexes was characterized by X-ray photoelectron spectroscopy (XPS) using a VG, ESCA-LAB Mk II with a non-monochromatized Al K $\alpha$  source ( $h\nu = 1486.6$  eV). The energy calibration for a charge correction in the spectra was made using the C1s peak. The FTIR spectra of the dried IP6 complexes were measured using KBr disks. Each disc was composed of powders consisting of IP6:KBr $\sim$ 1:100. The spectra were recorded in the range of 400 to 1400 cm<sup>-1</sup>. Raman spectra were obtained using an NR-1800 triple Raman system with backscattering geometry using the SHG(532 nm) of a Nd:YAG laser as the excitation source. All measurements were carried out at room temperature. It was found that various kinds of Ag nanostructures were formed with additional metallic sources using the Ag-IP6. Ag nanostructures with the three-dimensional dendritic structures replaced by Cu and Mn, the two-dimensional dendritic structures replaced by CaSi<sub>2</sub> and Mg, the two-dimensional fractal structures replaced by Fe, Ti, Al and Ni, the particles replaced by SrSi<sub>2</sub> and the nanowires replaced by Mo and W were formed. It is noted that the IP6 plays an important role as a silver carrier agent to control the structure and morphology of the Ag nanostructures. In addition, the experimental results suggest that the structural evolution of the Ag-IP6 reacted with Cu takes place to form the Cu-IP6 complex. However, the reaction of Ag-IP6 with Al is not active.

The structural properties of the Ag nanostructures were examined, and the growth evolution of the nanostructures was discussed. The results would help us to understand the nanostructure formation by the reaction between natural organic materials and metals in nature.

Keywords: IP6, nanostructure, dendrite growth, silver

## Development and application of 3-D interferometer for analysis of the concentration field in protein crystal growth

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When the crystal is growing in a supersaturating solution, the solute concentration is decreasing towards the crystal/ solution interface because the crystal consumes solute in the solution as it grows. Due to this large vertical concentration gradient, buoyancy driven solutal convection develops. As a result, the distribution of concentration around the crystal become complicated compared to the case when there is no convection.

Thus, not only concentration gradient but also the flow and convection of the solution influences the state of the crystal surface. So that visualizing the whole concentration field of a crystal interface including convection is required.

There have been many reports concerning the measurement of the concentration field, but many of them were two-dimensional (2-D) observations, namely, the objects were observed only from one direction. The information obtained by the 2-D observations is integrated in average along the direction of the observation, so the local information, e.g., concentration distribution around the crystal-liquid interface, was not obtained.

To improve the disadvantage on the 2-D observation, a method of computer tomography (CT) has been adopted in this study. By using the CT method, we can reconstruct the information of the three-dimensional (3-D) concentration field around the growing crystal based on 2-D observations obtained from several directions (3-D observation).

In this study, 3-D measurement of the concentration field with convection and without convection around inorganic and protein crystals was carried out to reveal the concentration distribution over the crystal surfaces. Normal growth rate of the face from points to points are also measured to discuss the effect of concentration distribution on the surface.

Keywords: interferometer, lysozyme, convection

## Dependence of impurity adsorption on the step morphologies and growth rate of tetragonal lysozyme crystal

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High quality protein crystals are required to get the information of the 3-dimensional structure of protein molecules. Impurities, mainly dimer molecules, affect the quality of protein crystal strongly (Yoshizaki et al., 2006). In addition, it is known that the step morphology on {110} faces of the tetragonal lysozyme crystal is changed by impurities. Until now, a lot of space experiments were carried out to get high quality protein crystals under microgravity conditions (McPherson, 1993, etc.). However, the relevance between impurity effects and microgravity condition is not clear. In addition, the step morphology corresponding to the crystal external form is not observed in preceding studies.

We performed "in situ" observations under terrestrial environment and space environment using a tetragonal lysozyme crystal as the model protein. The purpose of this paper is to reveal "the influence of microgravity condition to the impurities adsorption on the {110} faces" and "the reason why the step morphology corresponding to crystal external form does not appear". We made it possible to observe the step morphology and to measure the face growth rate at the same time by using a Michelson type interferometer.

As a result of growth rate measurement, the face growth rate under microgravity condition was higher than that under terrestrial condition. An impurity works to suppress the growth rate of a crystal. Because the buoyancy-driven convection was suppressed under the microgravity condition, we assumed that the larger impurity-depletion-zone was formed around a crystal.

As a result of the observation of the step morphology, we succeeded in observing the lozenge shape step which was corresponding to an external form by a space experiment for the first time. In addition, the step morphologies were classified in four types. It is considered that the impurity adsorption on the crystal surface is different depending on the crystal orientation of the step.