

## Comet-like particle growth in Al-SiO

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When a metal was evaporated in an inert gas atmosphere, a vapor of the metal cooled and formed nanoparticles by collision with the inert gas molecules. The nanoparticles grow by coalescence growth and rise on a convection flow of the gas like a smoke. The nanoparticle production method is called a gas evaporation method.

SiO consists of Si and SiO<sub>2</sub>. Metal nanoparticles covered with an amorphous SiO layer can be produced by evaporating a mixture powder of the SiO and a metal. However, comet-like particles were grown in the rising smoke using a few kinds of metals<sup>1)</sup>. In the case of Cr-SiO particle produced by the gas evaporation method, Si was dissolved in a Cr drop at a high temperature region in a smoke. The Si dissolved in the Cr drop was crystallized by supersaturation on cooling process. The Si crystal grew like a tail and the Cr drop became CrSi<sub>2</sub> crystal like a core of comet-like particle. The comet-like particle grew around the eutectic point between Si and CrSi<sub>2</sub>. Thus, the comet-like particle grew like a VLS mechanism.

Since Al has a eutectic point with Si, the comet-like particle growth was expected using a mixture powder of Al and SiO. Production of the comet-like particles was tried by the gas evaporation method.

Comet like-particles were produced by evaporation of Al and SiO mixture powder in Ar gas 1.0×10<sup>4</sup> Pa. The particles were observed by TEM, and analyzed by EDS. It was found that a core part of the comet-like particle consisted of Al or Al and Si, a tail part consisted of Al and O by EDS analysis. ED patterns of the particles indicated that structure of the core part was Si and Al crystals, and the tail part was Al<sub>2</sub>O<sub>3</sub> single crystal. Composition of Al and Si in the core part depended on the ratio of Al and Si in the mixture powder. The tail part structure was always Al<sub>2</sub>O<sub>3</sub> in every composition. The comet-like particles were grown like a VLS mechanism with SiO<sub>2</sub> reduction and Al oxidation.

1) C. Kaito et.al, J. Crystal Growth **200** (1999) 271.

Keywords: Nanoparticle, Whisker, Al, Si, Al<sub>2</sub>O<sub>3</sub>, TEM

## Infrared spectra during the growth of free-flying nanoparticles and its application to unidentified infrared bands

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Condensation of refractory materials is the first step of material evolution accompanying with stellar life. Though metals composed of refractory materials are not abundant elements in universe, it becomes relatively dominant at the region close to photosphere at high temperature and condensed to be a dust of refractory material. The first condensate becomes substrates for heterogeneous nucleations of subsequently condensed materials, such as magnesium silicate, at lower temperature. Therefore column density and size of first condensate decide subsequent dust evolution around late type giants. Oxygen rich M-type Asymptotic Giant Branch (AGB) stars are often observed with a 13 micron meter feature caused by a refractory material (e.g. DePew et al., 2006). The origin of the 13 micron meter feature has been theoretically explained by morphological effect of corundum (?-Al<sub>2</sub>O<sub>3</sub>). However, the 13 micron meter feature has not been demonstrated experimentally and has been remained as an unidentified infrared band so far. Understanding of the formation process of the origin of the 13 micron meter feature may give us the starting point of material evolution.

Infrared (IR) spectra of mineral samples have usually been measured after embedded into a KBr pellet. Then, the peak positions of a sample are shifted to the longer wavelength by medium effects of surrounding KBr (e.g. Tamanai et al., 2009). Our direct measurement method of free-flying nanoparticles is able to solve this problem and also is avoidable agglomeration of the samples, which dilute characteristic features caused by morphological effect, and contamination of the fresh surfaces of synthesized samples by exposure to air. Bulk crystal forms dangling bonds on their surface in vacuum. However, the dangling bonds changes when it will be in a KBr pellet. In case of nanoparticles, its surface area per volume becomes extremely large compared to that of bulk. It means that the contribution of a dangling bond on the surface of nanoparticles is not able to neglect to features in IR spectra. In these reasons, we started a new project, production of free-flying nanoparticles and observation of its infrared spectra. Here, we will describe the method and focus on the origin of the 13 micron meter feature.

Free-flying nanoparticles of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were produced by the gas evaporation method, and condensation processes of the refractory materials were examined using our new technique, free flying nanoparticles method with Fourier-transform infrared spectrometer. Condensed materials were analyzed by transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDS). In-situ measurement of IR spectra during condensation revealed the difference of the features in the IR spectra between primal condensates and adequately cooled samples as nanoparticles flow. Their IR spectra have a tendency of that primal condensates showed broader feature and the nanoparticles far from the evaporation source showed sharper feature. It may be a result of secondly nucleation from amorphous or molten particles formed by homogeneous nucleation from vapor phase.

As astromineralogical implication, TiO<sub>2</sub> nanoparticles with rounded edges have been proposed as a possible candidate for the 13 micron meter feature theoretically (Posche et al., 2003). The spectrum of TiO<sub>2</sub> nanoparticles showed the accordance of peak position with the theoretically predicted spectra.

## Impedance and light scattering measurements of calcite nucleation in microgravity of a rocket experiment

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### Introduction

It has been demonstrated for many years that the crystal growth experiments of calcite under microgravity conditions have provided new understandings of its crystallization processes as follows. Liu et al. (2000), Liu and Tsukamoto (2002) described the CaCO<sub>3</sub> nucleation under gravity and microgravity conditions using a parabolic flight experiment, especially, using the light scattering measurements. They found that lack of the gravitational sink in solution leads an elimination of a convection under microgravity indicating heterogeneous nucleation process. More recently, Maruyama et al. (2006) studied surface tension between solution (Aspartic acid-Asp) and calcite using light scattering methodology under microgravity provided by parabolic flights. They concluded that the calcite crystals from the Asp system grow faster than pure system. However, these authors were not able to get a relatively long microgravity conditions as they used the parabolic flight experiment giving 20 sec duration only.

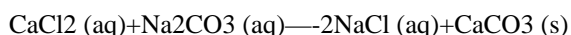
Here, we present preliminary results of CaCO<sub>3</sub> crystallization under a rocket experiment giving five minutes low-gravity duration. It is a purpose of this study to understand more about the transition of crystalline and amorphous states of carbonates as well as determination of the heterogeneous and homogeneous nucleation by means of impedance and light scattering measurements.

### Experimental Procedure

The calcite experiment (CAL) has a cell system containing total of 16 channels for the solutions (0-11) and for test (12-15), which was developed by Takasago Electric Inc for this study. The cell has special syringe pumps and valves, which are able to introduce the solutions simultaneously into the cell at the moment when microgravity is started.

Solutions were produced by dissolving calcium chloride (CaCl<sub>2</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in the double-distilled water (ultrapure water) with various mixed concentrations as follows: 2, 2.5, 2.75, 3, 3.2, 3.4, 3.6, 3.8, 4, 4.25, 4.5 and 5 mM.

CaCO<sub>3</sub> solutions were prepared after the mixtures of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions under the microgravity environment, which was based on the following chemical reactions.



### Results and Discussion

As a function of increasing concentration, there is a systematic increase of the impedance intensity (in unit of micro Amper) among 7 selected cells, which are a good agreement with the light scattering data, too. Compared to data obtained at the laboratory, rapid crystallization (around 1 sec) occurs at relatively high concentrations of 4, 4.5, and 5 mM solutions of the rocket experiment. Other cells (at medium or low concentrations of 3.8, 3.6, 3.2, and 2.25 mM) show relatively low induction time.

Supersaturation of the CaCO<sub>3</sub> solutions were calculated by using a phreeqc interactive software, which was based on inputs of average temperature (22.5 C) in the chamber, pH (10.5) and number of Ca and CO<sub>3</sub> ions as well as the estimated induction time in sec.

Consequently, supersaturation data indicate a homogeneous nucleation in our microgravity experiment as it was suggested by Liu et al. (2000) and Liu and Tsukamoto (2002).

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Keywords: calcite, microgravity, nucleation, sounding rocket, light scattering, impedance

## The electrostatic interaction between charged particles in small-number clusters for the colloidal crystallization

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Colloidal crystals are regular arrays formed by self-assembly of charged particles in suspension. In self-assembly, the interaction between particles plays an important role. The interaction between particles is explained by DLVO theory, which predicts a purely repulsive electro-static interaction between the particles. In contrast, a number of experimental evidences such as void formation suggest the existence of a long-range attractive force between charged particles.

Many studies have been carried out to measure the interaction of charged colloids in the equilibrium system. However, the existence of the long-range attractive force has not been confirmed yet. To understand the interaction of colloids deeply, a new experimental approach which is different from the former is needed.

As the new experimental approach, I observed the dynamics of a small-number cluster in the non-equilibrium system. I prepared a regular-hexagonal colloidal cluster composed of seven polystyrene particles in dilute dispersions by using holographic optical tweezers. Due to Brownian motion of each particle, a disordering arises in the hexagonal structure with time progresses. If some interaction force exists between particles, the disordering process will be different from what assumed the Brownian motion only. I defined the cluster lifetime as the time when the colloidal cluster does not satisfy the condition of a regular-hexagon. I measured the lifetime under different experimental condition (salt concentration of colloidal dispersions) and considered the interaction which works between colloidal particles (repulsive or attractive force).

From the experimental results, I found that the cluster lifetime became maximum at a certain salt concentration. In addition, the average distance between particles when the cluster collapsed was almost independent of the salt concentration within the experimental error. These results suggest the existence of some interaction between particles.

To consider the magnitude and direction of the interaction force, I carried out numerical calculations of the process that the cluster collapsed by Brownian dynamics (BD) method. As the interaction between particles, I considered three cases: DLVO, Lenard-Jones and Sogami-Ise potentials. The DLVO potential includes only the force of repulsion: on the other hand, the others include the force of repulsion and long-range attraction. In the numerical results using the DLVO potential, the cluster lifetime got longer depending on potential parameters. Simultaneously, the average particles distance when the cluster collapsed increased. On the contrary, in the results using Lenard-Jones and Sogami-Ise potentials, the average particles distance did not change with the increase in the lifetime.

These results suggest the existence of the long-range attractive interaction between charged colloidal particles.

Keywords: electrostatic interaction, small-number clusters, non-equilibrium system, optical tweezers, Brownian dynamics method

## Role of impurity on oscillatory growth and growth hysteresis of crystals

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Crystals characterized by oscillatory zoning show a quasi-cyclic alternation in the chemical composition in the growth direction, from a few tens of nanometers to several tens of micrometers in thickness. Such mineral zoning is a common phenomenon in magmatic rocks, hydrothermally altered rocks, mineralized rocks, and carbonate sequences. Oscillatory zoning may originate from external fluctuation or an intrinsic mechanism. In the first case, oscillatory zoning is induced by periodic changes in external growth conditions such as temperature, pressure, and solution composition. In the second case, the complex diffusion-attachment processes at the solution-crystal interface is considered to result in oscillatory zoning even under stable growth conditions. Some experimental studies have reproduced oscillatory zoning in the absence of external fluctuation, suggesting that the intrinsic mechanism plays an important role in some crystallization systems.

An important factor that affects the crystal growth kinetics is impurity, which is known to inhibit crystal growth. Pinning is a well-known effect of impurities on the kinetics of crystal growth in solution. Step advancement is pinned (or stopped) by impurities at the points of adsorption on the crystal surface. The step is forced to curve; the advancement velocity of the curved step is reduced by the Gibbs-Thomson effect. The time-averaged step velocity decreases with an increase in the density of adsorbed impurities and a decrease in supersaturation at the crystal surface. The pinning mechanism has been discussed successfully for various crystallizing systems with different impurities. It also accounts for the growth hysteresis, namely, two different growth velocities are observed at a given supersaturation, depending on the change in supersaturation (decrease or increase). However, the role of impurities on oscillatory growth has not been modeled on a physical basis to date.

We consider the adsorption and desorption of the impurities on the growing crystal surface along with the pinning mechanism. If the steps barely pass beyond a certain area on the crystal surface, the adsorption and desorption of impurities reach an equilibrium state (Langmuir isotherm). In contrast, repeated passage of steps shortens the exposure time of adsorption sites for impurities, and this tends to decrease the density of the adsorbed impurities. Frequent step passages will result in less impurities at the surface, as if the crystal surface is swept by the advancing steps. Because of impurity sweeping coupled with pinning, there is a potential feedback on the change in the step velocity through the change in the impurity density. The feedback loop causes periodic oscillation of the step velocity.

We propose a new mechanism of oscillatory growth and growth hysteresis based on step pinning by impurities adsorbed on the growing crystal surface. This model is very simple and is based on physically clear assumptions. The range of supersaturation over which the growth hysteresis appears is given by definite physical parameters such as step free energy, number density of the adsorbed impurities, and timescale of impurity adsorption. This mechanism is robust in the crystallization system from solution with existence of impurities.

Keywords: Crystal growth, Oscillatory growth, Growth hysteresis, Pinning mechanism, Impurity

## ”In-situ” observation of the normal growth rate and surface concentration field of a lysozyme crystal under microgravity

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Since the convection in solution is restrained in microgravity environment, the rate of the supply of a solute to the crystal surface is governed by diffusion. Therefore, it has been widely believed that the crystal growth rate decreases compared with the case on the ground. The generation of defects is also believed to be restrained due to shortage of impurities on the crystal surface. As the result, it was expected that the quality of the crystal is improved in microgravity. But actual growth rate of protein crystal was equal or increased in microgravity environment is obtained in the protein crystal growth experiment using a satellite. However, in order to have such a discussion, we have to measure the normal growth rate of the crystal precisely under microgravity where convection is controlled.

We carried out the microgravity experiment in the International Space Station (ISS) that gives ideal environment without convection. A protein crystal grows within the specially designed cell, whose temperature is controlled with two interferometers to clarify the relationship between the growth rate and surrounding environment.

The ”in-situ” observation of the concentration field around the crystal and the measurement of normal growth rate of (110) surface were carried out by using the Mach-Zehnder and the Linnik interferometer, simultaneously. The sample used for the experiment is a tetragonal lysozyme (solution concentration 30 mg/ml, 50 mM Acetic acid buffer pH4.5, NaCl 2.5%). The crystal growth cell was conveyed to ISS after enclosing a seed crystal and solution on the ground. The cell is made of silica glass and has enclosed a seed crystal and a couple of glass with the inside. The glass serves as a reference, when measuring a growth rate with the interferometer. The seed crystal was chemically fixed to avoid deterioration and dissolution by temperature elevation during transportation to ISS. A seed crystal was prepared on the wall of the cell with the direction of that (110) surface became to be perpendicular to the optical path of the Linnik interferometer. Peltier devices control the temperature of the cell and solution. Supersaturation of the solution was controlled by the change of temperature.

Concentration gradient at the interface under the microgravity was observed and had a gentle slope compared with that obtained under gravity. But concentration has fallen considerably to bulk at the interface. Moreover, the time dependence of the interface concentration profile was fluctuated irregularly.

Compared with the case under gravity, growth rate of the lysozyme crystal under micro gravity became larger about 30% at the maximum. The critical supersaturations for two-dimensional nucleus formation were obtained from the supersaturation dependences of the growth rates and were 1.2 under micro gravity and 0.7 on the ground. Under micro gravity, two-dimensional nucleus formation was suppressed and spiral growth becomes predominant in comparison with the case under gravity. Even if the temperature of solution was maintained at constant, the crystal growth rate was fluctuated. The supersaturation of the interface was also changed by time, but the tendency does not always accord with fluctuation of the growth rate.

These observations suggest that not only the concentration change at the interface but also growth kinetics of crystal surfaces and the change of the angle of a growth hillock cause fluctuation of the growth rate of the crystal.

Keywords: lysozyme, interferometer, crystal growth



## Smectite dissolution behavior observed by Internal refraction interferometry with an enhanced PSI.

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Use of smectite clay has widely spread and been diversified in many fields such as construction, agriculture, environmental remediation, etc. Its stability is important research issue from the points of views of not only weathering science but also industrial use. Dissolution rate of smectite has been investigated in laboratory experiments for some decades. Most of these investigations were conducted to use the powdered smectite sample, batch or flow-through experimental setup, and solution analysis method. We developed an enhanced PSI with white light source which was specially designed to improve the observation capability for very slow kinetics of mineral in solutions. In addition the we developed a novel technique of Internal refractory interferometry by using the PSI, which allowed us to measure the dissolution rate focused only crystal part of smectite. In this study, the laminated structure of smectite crystal on the dissolution is discussed.

Keywords: interferometry, internal refraction interferometry, smectite, dissolution, dissolution rate

## Microgravity experiment of homogeneous nucleation of iron from vapor phase using the sounding rocket S-520-28

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Nucleation theories have been used to understand the condensation sequence, number density and size of cosmic dust in a gas outflow of dying stars or a gas plume after shock wave heating in the primitive solar nebula. However, it has been well known that nucleation rates obtained by classical nucleation theory and by experiments have a large difference. In addition, most of the physical parameters of nanometer sized particles are unknown. Therefore, it is still not successful to explain the characters of cosmic dust by a nucleation theory. To determine the physical parameters of nanoparticles and evaluate nucleation theories, we constructed an in-situ observation system of temperature and concentration during homogeneous nucleation in vapor phase using interferometry.

Nanoparticles are formed from a supercooled vapor after evaporation by electrical heating in a gas atmosphere. Using the new system, we succeeded to determine surface free energy and sticking probability of manganese nanoparticle from timescale for gas cooling and condensation temperature based on nucleation theories (Kimura et al. 2012). In this laboratory experiment, convection of gas atmosphere caused by thermal heating generates heterogeneity of nucleation environment, such as temperature and concentration profiles around evaporation source. If same kinds of experiments are performed in microgravity, evaporated vapor defuses uniformly and the temperature profile becomes concentric around the evaporation source. As the result, nucleation will occur at the same condition. Then, we can obtain physical properties with relatively smaller error bars and then we may be able to evaluate nucleation theories more precisely. Therefore, we did a microgravity experiment using the sounding rocket S-520-28 launched on December 17th, 2012.

We prepared specially designed Mach-Zehnder-type interferometers with an evaporation chamber and camera recording systems to fit the space and weight limitations of the rocket. Three systems, named DUST 1 to 3, with same configuration except evaporation source and gas pressure in the chamber were installed into the nosecone of the rocket. The evaporation source and gas atmosphere were tungsten and gas mixture of oxygen (4000 Pa) and argon (36000 Pa) for DUST 1, iron and argon (20000 Pa) for DUST 2, and iron and argon (40000 Pa) for DUST 3. The experiments were run sequentially and automatically started from 100 s after launch of the rocket. The evaporation source of iron was electrically heated in Ar gas of 20000 and 40000 Pa under microgravity. Evaporated iron vapor was diffused, cooled and condensed in the gas atmosphere. The temperature and concentration at the nucleation site are determined from the movement of the fringe in the interferogram. Here, we will show the first results of the homogeneous nucleation, such as supercooling, and the physical properties of iron nanoparticles based on nucleation theories.

Keywords: Nucleation, Dust, nanoparticle