Japan Geoscience Union Meeting 2012
(May 20-25 2012 at Makuhari, Chiba, Japan)

MIS24-01 Room:202 Time:May 22 13:45-14:00

Crystallographic analyses of exoskeletal calcium carbonate in *Armadilidium vulgare* (Crustacea, Isopoda)

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Calcium carbonate ($CaCO_3$) is one of the most major biominerals, found in many organisms such as mollusks, arthropods, and echinoderms. Previously, it is thought that biotic $CaCO_3$ crystals are precipitated from a supersaturated solution directly. However, in recent years, existence of amorphous calcium carbonate (ACC) as a precursor phase of calcite or aragonite has been suggested in some organisms, but this is still not certain. In this study, we have investigated a terrestrial isopod, *Armadilidium vurgare*, because previous works indicated by Raman spectroscopy that at least a portion of calcite is transformed from ACC in its exoskeleton. We mainly investigated crystallography of calcium carbonates, using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) with Electron Backscatter Diffraction (EBSD), Transmission Electron Microscopy (TEM) to understand the characteristics ACC-mediated calcite. Focused Ion Beam (FIB) was used for the preparation of TEM samples.

FIB-TEM observation indicated that the outermost layer (distal layer) of the exocuticle consists of well-crystallized platy calcite single crystals of ˜0.5 micron thick and several micron in width. SEM-EBSD analyses of the distal layer indicated that scale-like domains on the surface of the exocuticle correspond to calcite single crystals. The *c*-axes of calcite in the distal layer are basically parallel to the anteroposterior axis, but varied from the complete parallelism to standing by ˜50^o from the surface. On the other hand, the inner layer (transition zone) of the exocuticle contains spindle-shaped crystals of ˜0.5 micron and organic matrices. Electron diffraction (ED) indicated that the crystals are also calcite. TEM imaging, ED and Energy Dispersive X-ray Spectroscopy (EDS) analyses suggested that the endocuticle under the transition zone does not contain crystalline calcium carbonates, but ACC and organic matrices. TEM-EDS analyses indicated that calcite in the distal layer was almost free of phosphorous which can act as an inhibitor of the crystallization of ACC, whereas a certain amount of phosphorous was detected in the transition zone. Phosphorous is the most abundant in the endocuticle, probably to stabilize ACC.

From these results, it is inferred that calcite in the distal layer was precipitated on organic matrices from solution directly, and that in the transition zone was crystallized from the ACC precursor.

Keywords: calcite, ACC, SEM-EBSD, FIB-TEM, phase transition

MIS24-02 Room:202 Time:May 22 14:00-14:15

Pressure-induced crystallization of amorphous calcium carbonate

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Amorphous calcium carbonate (hereafter ACC, $CaCO_3nH_2O$), a metastable phase of calcium carbonate, contains variable amounts of water molecules and is a precursor of crystalline calcium carbonate, such as calcite, aragonite and vaterite. ACC immediately crystallizes in an aqueous solution or a humid condition. In nature, ACC stably exists only in biominerals, produced by living organisms. Crystals with complicated shapes are formed via ACC in biomineralization. Understanding crystallization of ACC will contribute to well understandings of the fundamental properties of ACC such as stability, structure, and mechanism of biomeralizaation. It is already known that ACC crystallizes by heating (e.g. Koga et al., 1998). On the other hand, stability of ACC at high pressure is unknown. In general, it is known that some amorphous materials show structural changes and pressure-induced crystallization by pressure. This study newly investigated pressure response of ACC at room temperature.

ACC was synthesized by the following procedure; aqueous solutions of 0.1 M $CaCl_2$ and 0.1 M Na_2CO_3 at 0 degree C were mixed, and the obtained suspension was filtered and dried in vacuum condition at room temperature. Vacuum drying was conducted using a diaphragm pump (about 10^2 Pa) for one day. The water content of ACC was estimated from water loss in TG-DTA. The compression experiment on ACC was conducted using a piston-cylinder and a hydraulic press. The applied pressure was kept in the range of 0.08-0.8 GPa for 10 min in the each run. The appearance of crystalline phases of calcium carbonate was characterized by power XRD patterns of as-grown ACC and the samples recovered from high pressure.

Chemical formula of the obtained ACC was $CaCO_3 1.5H_2O$, which is consistent with previous studies. XRD patterns of the ACC (n = 1.5) and its pressured samples demonstrated that ACC transforms to crystalline calcium carbonate (calcite and vaterite) at pressures greater than 0.2 GPa at room temperature. The crystallization pressure of ACC is the lowest in amorphous materials reported before: for instance, amorphous alloys, silicon, and so on.

It is expected that the properties, including pressure response, of ACC depend on its water content. For comparing pressure response between ACCs with different water contents, ACC with less water content was necessary to be synthesized. We tested the possibility that the water content of ACC can be controlled by changing vacuum condition. For this purpose, additional evacuation for another day was applied to the ACC ($CaCO_1 1.5H_2O$) using a turbo-molecular pump (about 10^{-3} Pa). As a result, water content of the obtained ACC was substantially decreased ($CaCO_3 0.6H_2O$). XRD patterns of the ACC (n = 0.6) and its pressured samples indicated that ACC (n = 0.6) crystallized at pressure over 0.6 GPa, which is notably higher than the transition pressure of ACC (n = 1.5). These results suggest that the water contained in ACC plays an important role in pressure-induced crystallization of ACC.

Keywords: amorphous calcium carbonate, pressure-induced crystallization

MIS24-03 Room:202 Time:May 22 14:15-14:30

Quantitative XRD analysis of {110} twin density in biotic aragonites

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{110} twin densities in biotic aragonite have been estimated quantitatively from the peak widths of specific reflections in powder X-ray diffraction (XRD) patterns, as well as direct confirmation of the twins using transmission electron microscopy (TEM). Influence of the twin density on the peak widths in the XRD pattern was simulated using DIFFaX program, regarding (110) twin as interstratification of two types of aragonite unit layers with mirrored relationship. The simulation suggested that the twin density can be estimated from the difference of the peak widths between 111 and 021, or between 221 and 211 reflections.

Biotic aragonite in the crossed-lamellar microstructure (three species) and nacreous microstructure (four species) of molluscan shells, fish otoliths (two species), and a coral were investigated. The XRD analyses indicated that aragonite crystals in the crossed-lamellar microstructure of the three species contain high density of the twins, which is consistent with the TEM examination. On the other hand, aragonite in the nacre of the four species showed almost no difference of the peak widths between the paired reflections, indicating low twin densities. The results for the fish otoliths were varied between the species. Such variation of the twin density in biotic aragonites may reflect different schemes of crystal growth in biomineralization.

Keywords: {110} twin, aragonite, biomineralization, DIFFaX, TEM, X-ray diffraction

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MIS24-04 Room:202 Time:May 22 14:30-14:45

Influence of intracrystalline organic macromolecules in shells on the crystal growth of calcite

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Biominerals often possess well-regulated structures with superior properties. Such superiority may be ascribed to the fact that biominerals are not pure inorganic crystals because they contain a certain amount of organic matter. Among the organic matter, ”intracrystalline” organic macromolecules such as proteins and polysaccharides have been studied recently, owing to their important roles during crystal growth. Nanoscopic investigation is essential to understand the interaction between crystals and intracrystalline organic macromolecules because the sizes of the organic macromolecules estimated from their molecular weights are several to dozens nanometers.

We are investigating mollusk shells, especially focusing on the relationships between calcite crystals, which is one of the polymorphs of calcium carbonate, and intracrystalline organic macromolecules. Transmission electron microscopy (TEM) with electron energy-loss spectroscopy (EELS) identifies the intracrystalline organic macromolecules, and X-ray diffraction (XRD) evaluates macroscopic properties of the crystals. Using these nanoscopic and macroscopic techniques, we revealed that the distribution of the intracrystalline organic macromolecules affects the microstructure of the crystals. In the prismatic structure in a pearl oyster (*Pinctada fucata*), which is composed of columnar calcite crystals, intracrystalline organic macromolecules are distributed inhomogeneously, which causes small misorientations and local lattice strain. On the other hand, the organic macromolecules in the prisms in a pen shell (*Atrina pectinata*) are distributed homogeneously in the crystals, and local lattice strain is rarely observed. We thought such difference is originated from the different affinities of the organic macromolecules to the calcite crystals. Therefore we conducted calcium carbonate crystallization *in vitro* with EDTA (ethylenediaminetetraacetic acid) soluble extract from the prisms. It was found that the organic macromolecules in the extract from *P. fucata* and *A. pectinata* are incorporated differently in calcite. Furthermore, we are characterizing the organic molecules in the extract using molecular biological techniques to consider their interaction with their host calcite crystals.

Keywords: organic macromolecules, calcite, biomineral, TEM

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MIS24-05 Room:202 Time:May 22 14:45-15:03

Dynamics of organic molecule adsorption on calcium carbonate calcite surface: a molecular dynamics study

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Crystal growth of $CaCO_3$ in organisms is controlled by organic molecules, such as polymers, proteins and peptides. Elucidating the mechanism of the $CaCO_3$ growth control by organic molecules is of particular importance for understanding of the mechanism of biomineralization, crystal morphology technologies and the development of novel organic/inorganic hybrid materials. However, it is quite difficult to analyze the structure and dynamics of water and organic molecules at a $CaCO_3$ crystal surface in detail by experimental means. Thus, our understanding of the mechanism of $CaCO_3$ crystal growth control by organic molecules is still poor.

Recently, we have started computer simulation studies on the mechanisms of $CaCO_3$ crystal growth and the control of it by impurities. One of them is a molecular dynamics (MD) simulation study of the adsorption of aspartic acid (ASP) on the surface of $CaCO_3$ calcite. At the presentation, I will talk mainly about this MD simulation study.

The simulation was carried out for both (104) and (110) faces of $CaCO_3$ calcite. Intermolecular interactions acting on $CaCO_3$ and H_2O are calculated using simple Ca^{2+}, ${CO_3}^{2-}$ and H2O models in which the Coulomb potentials between charges and the short-range interactions between atoms are assumed. The intermolecular interactions acting on ASP was calculated using the CHARMM force field. Temperature was set at 298 K.

Simulation results indicated the formation of a few H_2O molecular layers on the (104) face. In each layers, H_2O molecules were arranged in an ordered state. However, such layers did not appear on the (110) face. It proved that the formation of the layers strongly influences the adsorption conformation of ASP at the calcite surface. For the (104) face, ASP did not adsorb directly onto the face, but a H_2O molecular layer was sandwiched between the adsorbed ASP and the face. Moreover, careful analysis of the free energy of ASP adsorption suggested the existence of several metastable adsorption conformations at the face. Details of the 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: biomineralization, computer simulation, crystal growth, surface and interface, calcite, aspartic acid

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MIS24-06 Room:202 Time:May 22 15:30-15:48

Preparation of Core-Shell Type Organic/Metal Hybridized Nanocrystals and Their Optical Properties

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Organic nanocrystals (NCs) are in the mesoscopic phase between a single molecule and the corresponding bulk crystals, and are expected to exhibit peculiar optical properties, depending on crystal size and shape. Well-defined, i.e., size- and shape-controlled, organic NCs could be prepared successfully from pai-conjugated organic and polymer compounds by developing the reprecipitation method. Interestingly, organic NCs exhibited the size-dependence of linear optical properties (extinction and fluorescent emission spectra), which is speculated to be caused not by so-called quantum size effect in semiconductor quantum dots by but thermal softening of nanocrystal lattice, due to increase in specific surface area with decreasing crystal size. Namely, the effective pai-conjugation length would decrease, owing to disordered and strained nanocrystal lattice, and then the band gap (or HOMO-LUMO gap) would widen with decreasing crystal size.

In this presentation, recent progress on hybridized organic NCs and ordered array structure of encapsulated organic NCs will be introduced in detail for optically functional materials toward next-generation organic device application. In other word, hybridization is one of the main and important objectives in current material science. Our attention is now focused on core-shell type hybridized organic NCs, which seem to be the best suited nanostructure for the occurrence of novel optoelectronic properties and photonic function induced by core-shell interface interaction. Polydiacetylene (PDA) NCs (core) and Ag nanoparticles (NPs) (shell) hybridized NCs could be fabricated reproducibly by the development of visible-light-driven photocatalytic reduction method. PDA is one of the most promising candidates in organic nonlinear optical (NLO) materials, which shows the large third-order NLO susceptibility and highly speed of optical response in femto-second order. Actually, the value of the susceptibility from PDA NCs (core) has been multiplied evidently, due to the enhancement effect of optically electric field induced by localized surface plasmon resonance from Ag NPs (shell). The present reduction process could proceed easily, being independent of core size and shape, when the redox potential of metal ion (or metal complex) should be located between conduction band and valence band in pai-conjugated polymer such as PDA. So some various hybridized NCs could be produced in the similar manner, for example, rod-like and fibrous PDA NCs, polyalkylthiophene NPs as a core material, and Pt NPs and Au NPs as a shell material. But, the subsequent chemical reduction process was performed at the same time, when Au NPs (shell) is prepared.

On the other hand, it should be necessary to arrange and integrate organic NCs, including hybridized ones, on a substrate so as to receive and transmit input- and output-information signals by electronically and/or optically accessing to organic devices. So, encapsulations of organic NCs, patterned substrate, and tapered cell method have been employed suitably to fabricate and control ordered array structure of organic NCs on a substrate. First, mono-dispersed polystyrene microsphere (PSMS) was used as a model of encapsulated (and hybridized) NCs, and some beautiful ordered array structure could be formed on the patterned substrate by optimizing the size of PSMS and pattern design. Especially, so-called Kagome Structure composed of PSMSs could be fabricated for the first time, which structure is said to provide the confinement effect of light propagation and a kind of photonic crystals. In addition, it has become possible to build-up the order array structure consisted of encapsulated semiconductor NPs and PDA NCs produced by emulsion polymerization process for optoelectronics and photonics devices application.

Finally, the future scope in the relevant fields of optoelectronics and photonics will be discussed in brief.

Keywords: Organic Nanocrystal, Hybridized Nanocrystal, Reprecipitation Method, Nonlinear Optical Property, Localized Surface Plasmon Resonance, Visible-Light-Driven Photocatalytic Reduction Method

MIS24-07 Room:202 Time:May 22 15:48-16:03

Crystal Growth in Colloids Due to Charge Induced Crystallization

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Submicron sized charged colloidal particles dispersed in water self assemble into ordered crystal structures at sufficiently strong electrostatic interparicle interactions. Here we report the charge induced crystallization in dilute aqueous dispersions of colloidal silica by varying pH, and unidirectional crystal growths of the silica colloids under gradients of pH and temperature.

Keywords: colloid, charged colloidal particle, colloidal crystal, crystal growth, solid liquid interface, silica particle

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MIS24-08 Room:202 Time:May 22 16:03-16:18

Molecular Dynamics Study of Aqueous solutions: solubility calculation and crystallization process

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Aqueous solutions are fundamental to chemistry, biology, and geology. When an aqueous solution is in high pressure and high temperature conditions, the aqueous solution becomes supercritical. It is known that the behavior of supercritical region is different from that of ambient region; however, the experimental study is very difficult. Molecular Dynamics (MD) is useful tool to observe a system in such conditions. Solubility which is one of most significant properties can be calculated with MD. Solubility calculation with MD has mainly two approaches: the free energy calculation and the direct calculation, which are thermodynamic approach and kinetic approach, respectively. The thermodynamic approach, the free energy calculation, calculates separately the values of chemical potential in solution phase and solid phase. This approach has less calculation cost and less information. The kinetic approach, the direct calculation, employs salt-solution combined system. This approach has much information which includes relaxation process. However, there is no knowledge whether two approaches produce the same solubility value or not. Thus, it is, of essential importance, to test by using two different approaches. We firstly have calculated the solubility of ambient system with the two approaches and concluded two approach had good agreement. This work will contribute to the computational chemistry field as well as solubility in supercritical region. The study at supercritical conditions is undergoing.

Keywords: sodium chloride, solubility, crystallization, molecular dynamics, supercritical solution, interface of solid

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MIS24-09 Room:202 Time:May 22 16:18-16:33

Growth rate and specific surface free energy of synthesized quartz single crystal

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The specific surface free energy of quartz single crystal was determined by contact angle of water and formamide droplets on the crystal surface, and compared with the morphology of the crystal. The growth rate of the quartz crystal can be regarded as a function of the experimentally obtained specific surface free energy. The distriburion of the specific surface free energy indicates the existance of negative step free energy.

Keywords: crystal growth, crystal surface, free energy

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MIS24-10 Room:202 Time:May 22 16:33-16:48

In-situ observation of crystal growth from undercooled liquids using containerless technique

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We performed in-situ observation of crystal growth from the undercooled liquids of alloys and oxides using high-energy x-ray diffraction combined with the container-less technique . Using the method, we can see the various phase transformation from the undercooled liquids to the stable crystalline phases. From the observation results we discuss about the crystal growth mechanism from the undercooled liquids from the viewpoint of the correlation between liquid and crystal structures.

Keywords: crystal growth, supercooled liquids, levitation technique

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MIS24-P01 Room:Convention Hall Time:May 22 17:15-18:30

The effect of PO4 on vaterite formation and dissolution in solution

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Calcium carbonates are essential materials in biological beings as main component of hard tissue like shells. These calcium carbonate minerals are called as biogenic minerals. These minerals were formed from body fluid, which is a neutral-weak based solution, and the process is called as biomineralization. It is known that under neutral-weak based condition, amorphous calcium carbonate (ACC) is emerged from supersaturated solution as an initial solid phase and quickly transformed to vaterite by dynamic structural phase transition. Vaterite is intermediate and metastable phase. Calcite is formed later than vaterite, and as the calcite nucleates and grows further, vaterite begins to dissolve because of the following reason: calcite solubility is lower than that of vaterite, so solute concentration in solution drops below vaterite solubility with the growth of calcite. In this reason, in neutral-weak based solution, only calcite remains as the precipitate stably and other polymorphs will disappeared even if they precipitated at once.

However, in biological system, there were various metastable calcium carbonate polymorphs like ACC and vaterite that consist of biological structures. It is strongly suggested that some additives included in body fluid were controlling calcium carbonate nucleation and phase transitions. Especially, it was suggested that PO4, which is essential materials for biological systems acts a stabilizer of ACC and an inhibitor of calcite growth. However, there were little literature about PO4 effect on vaterite formation and dissolution. In this paper, we investigated the formation and dissolution process of vaterite PO4 containing from the incubation time for vaterite nucleation and polymorph change during precipitation.

We prepared supersaturated calcium carbonate solution containing PO4 ions by mixing CaCl2, Na2CO3, KH2PO4, NaCl and tris-aminomethane solutions. pH was buffered at 8.2-8.3 by tris-aminomethane to simulate body fluid. Concentration of Ca and CO3 ions were adjusted at 10 mM at initial. We adjusted concentration of PO4 ion at various values, 0-125 uM, to investigate dependence on PO4 concentration. We kept this solution at room temperature and atmospheric pressure with stirring to precipitate calcium carbonate. We sampled the precipitates every regular time intervals to observe their morphologies and to identify their phases by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Also, we monitored Ca ion concentration in solution by using Ca electrode to detect the timing of nucleation of calcium carbonate crystals.

In less than 10 uM PO4 systems, ACC particles of 10-100 nm in size emerged as an initial phase. With decrease of Ca ion concentration, vaterite spherulites of 0.5-5 um in diameter emerged. Incubation time till the detection of Ca ion concentration decrease elongated with increase of PO4 concentration as proportional to cube low of PO4 concentration, and reached about 1500 sec at 10 uM in PO4 concentration. Vaterite spherulites remained after 2 hours without collapsing. On the other hands, in more than 15 uM PO4 systems, there were no evidences for calcium carbonate crystalline nucleation till 2000 sec in Ca ion electrode and electron microscopy observation. As Ca ion concentration dropped after 2000 sec, small amount of vaterite spherulites and large amount of calcite crystals appeared. With proceeding time, the ratio of calcite to vaterite was increasing, and vaterite spherulites revealed halo structure. Suggesting dissolution of vaterite. Thus, it is suggested that PO4 act as an unstabilizer for vaterite.

In previous works, it was suggested that PO4 act as a stabilizer for ACC. This mechanism can be interpreted from our experiments as follows; PO4 inhibited to vaterite nucleation and maintain high calcium carbonate concentration in solution, so ACC survived from dissolution for a long time.

Keywords: vaterite, PO4, phase transition, additive effect

MIS24-P02 Room:Convention Hall Time:May 22 17:15-18:30

Development of an Advanced Phase-Shift Interferometry to measure dissolution rate and phenomena of insoluble minerals

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From the point of views of the safety of radioactive waste disposal, dissolution of bentonite as engineered barrier and/or rock system surrounding waste as natural barrier is one of the key issues. Nevertheless, the understanding of the dissolution mechanisms in dissolution of very insoluble minerals is still insufficient. Therefore, an advanced Phase-Shift Interferometry (PSI) was developed to resolve dissolution process on a molecular level. The advanced PSI is distinguished by the some features, such as white light source for illumination, large working distance of the object lens, and so on. It allows the direct, simultaneous, and high speed measurement of dissolution of minerals. This high speed and high resolution observation shorten the observation period, and decrease the influence of disturbance of experimental condition. These are strong advantages for understanding the dissolution mechanism. For example, biotite dissolution rate of the order of 1E-11 mol/m2/s was measured in the period of 4 days to 20 days by means of conventional method. It was measured by means of the advanced PSI within 12 hours.

Keywords: Phase-Shift Interferometry, insoluble mineral, dissolution rate, dissolution phenomena

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MIS24-P03 Room:Convention Hall Time:May 22 17:15-18:30

Direct observation of nucleation and dissolution processes in a solution using a TEM

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Since nucleation is a fundamental event to determine size, number and morphology of produced crystals, nucleation process must be clarified to form products efficiently. Direct approach to understand nucleation would be an atomic scale in-situ observation. A transmission electron microscope (TEM) may be a most powerful tool. Unfortunately, however, we can prepare limited experimental condition in a TEM and only have a few reports concerning in-situ observation of a nucleation process so far. In particular, since TEM needs a high vacuum, crystallization experiment in a solution was impossible. Recently, formation process of platinum nanoparticles from a solution was observed using a specially designed cell in a TEM [1]. Disadvantages of this noble method are difficulties of high-resolution observation and changing the temperature. Recently, we overcame the disadvantage by using ionic liquid, which has negligible vapor pressure and does not charge up by electron beam due to their relatively higher electron conductivity. Ionic liquid has been used for direct observation of organic materials such as protein and sea weed using mainly scanning electron microscope or occasionally TEM observations. Here, we report successful in-situ observation of nucleation, growth and dissolution processes of sodium chlorate in an ionic solution.

Supersaturated ionic solution of sodium chlorate was prepared on a TEM grid. After controlled induction time, sodium chlorate crystals nucleated and grew under TEM observations with an acceleration voltage of 200kV (Hitach H-8100 placed at the Tohoku University). Ionic solution could be observed stably under normal electron irradiation condition. Nucleated sodium chlorate crystals were floated with the Brownian motion. When two crystalline particles contacted, they fused together to be a larger single crystalline particle. Produced nanocrystals of sodium chlorate were heated up and were observed their dissolution process using a TEM with an acceleration voltage of 300 keV (H-9500 placed at the Hitachi Hitec). The nanocrystals were not only dissolved but also grown even in the totally dissolving system, i.e., most probably undersaturated condition.

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Keywords: Nucleation, nanoparticle, dust, in-situ observation, electron microscope, ionic liquid

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The growth mechanism of needle-like aragonite crystal

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Calcium carbonate ($CaCO_3$) is one of the most studied minerals among the barely soluble substances, since precipitation of $CaCO_3$ is a widely occurring process in biomineralization as well as in manufacturing process of industrial materials. For example, its needle-like crystals with high aspect ratios have been used as fillers to improve mechanical properties of paper and polymer materials [1]. To control the morphology or polymorph of $CaCO_3$ crystal, the effect of additives on the crystallization of $CaCO_3$ has been studied [2]. However, the growth mechanism of calcium carbonate crystals has been poorly understood yet. Understanding of the growth mechanism is important for constructing materials with morphology and function as we aim.

With respect to the needle-like crystals, two types of crystallization mechanism have been considered. One is VLS (vapor-liquid-solid) mechanism, which has been observed in formation of Si whisker [3]. Another is Frank mechanism with spiral dislocation, which is considered as a formation mechanism of NaCl whisker from solutions [4]. In this study, we synthesized needle-like aragonite crystals from solution. In order to understand the growth process of the needle-like aragonite crystal, we observed the tip of it in details by using electron microscopy.

We synthesized needle-like aragonite crystal by pouring Na_2CO_3 solution into the 40 ml of $CaCl_2$ solution with the rate of 1 mL min^{-1}. We stopped the inflow when the total volume of poured Na_2CO_3 solution reached 40 ml. The mixed solution was stirred at 300 rpm for about 3 h. The concentrations of $CaCl_2$ and Na_2CO_3 solutions are the same; we considered two cases of 0.005 and 0.05 mol/l. We controlled the temperature of solution at constant as 25, 50 and 80 deg C during precipitation. The morphology and the size of the precipitates were observed by scanning electron microscopy (SEM), and their crystalline phases were identified by X-ray diffraction (XRD).

The crystals obtained in the experiment were mainly needle-like aragonite and spherules of vaterite. The length of needle-like aragonite was about 2 -20 micrommeters. The aspect ratio was estimated from 5:1 to 20:1. For vaterite, the size was about 2-5 micrometers. The total amount of precipitated crystals definitely depended on the concentration of initial solutions: many precipitates for higher concentration and few precipitates for lower concentration. The reaction temperature obviously affected the crystalline phases; aragonite was mainly crystallized at 80 and 50 deg C, on the other hand, vaterite particles appeared at 50 and 25 deg C. The morphologies were also affected by the reaction temperature. Vaterite changed from circular disc to sphere according to the decrease of reaction temperature from 50 deg C to 25 deg C. It was also seen that the higher the reaction temperature, the larger the aspect ratio of needle-like aragonite.

By detailed SEM observation, we showed that the needle-like aragonite has multi-step on the tip, which seemed higher than monomolecular step. Based on the experimental results, possible growth mechanism of needle-like aragonite was proposed.

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Effect of bacteria on calcite precipitation

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Calcite precipitation with/without bacteria was studied in two fields; Ogachi and Matsushiro. At Ogachi, two types of bacteria were mixed with carbonated water and passed through a coloum filled with glass beads. Calcite precipitation was observed in one column. At Matsushiro, hot spring water saturated with carbonate was also passed through a column and aragonite was detected in the column.

Keywords: calcite, bacteria, precipitation, hot spring, rate

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The microgravity effect in colloidal phase separation

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Colloidal crystals are considered in the application to photonic crystals. The gravitational sedimentation method attracts great attention because of simplicity. It is thought that crystallization of colloidal crystals is caused by KirkWood-Alder transition because of the repulsive interaction. However, to the colloidal dispersions in the conditions of low particle concentration and low ionic strength, void structure was generated 1) or gas-liquid-solid phase separation occurred 2). These phenomena cannot explain by only the repulsive force. The facts suggested the existence of a long-range attractive interaction between particles in spite of their repulsive pair potential. So, these results are very important.

The colloidal phase separation which arises in a gravity sedimentation process was reported 3). After like-charged colloidal particles sediment on glass substrate, colloidal particles cause gas-liquid-solid phase separation. A long-range attractive interaction between particles is required in order to bring out this phenomenon. However, in this experiment, when the phase separation of like-charged colloidal particles occurs, particles are always close to a glass substrate according to the gravity effect. Therefore, the interaction which works between particle-particles or between glass substrate-particles may be influenced by the gravity. So, in order to eliminate gravity effect, we experimented under microgravity.

3 um polystyrene particles (Thermo scientific) were used. The density was 1.05 g/cm3. We compared the colloidal sample which was deionized one month or more by using Bio-Rad ion-exchanger resin and the untreated sample. Under the ground, the colloidal dispersion of 0.015 vol % was enclosed with the angle cell (10 mm x 10 mm x 47 mm), and 24 hours was settled. The angle cells were installed in the airplane. Then, the colloidal accumulations were observed in the microgravity environment about 20 seconds.

We measured the position change of colloidal particles. The diffusion coefficient by Brownian motion was calculated from these data. The diffusion coefficient of deionized sample was 0.082 um2/s and untreated sample was 0.137 um2/s. On the other hand, the diffusion coefficient obtained from the Stokes rule was 0.14 um2/s. The untreated sample was well in agreement with the diffusion coefficient obtained from the Stokes rule. When the value of a deionized sample and an untreated sample was compared, the direction of a deionized sample has a small value of a diffusion coefficient. In the deionized sample, we found a sign of the long range attractive interaction.

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Keywords: colloidal crystal, phase separation, microgravity, diffusion coefficient

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Theoretical analysis of atomic process on the growth surface

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In order to understand formation process of minerals, it is important to analyze the atomic process on the growth surface. First-principles calculation of the growth surfaces is useful for this purpose, and is often used for semi-conducting materials. Recent progress of computer technology would make it applicable for more complex system such as minerals, which will provide more realistic information for the mineral growth in the atomic scale.

Here, as an example of this kind of approach, incorporation process of nitrogen (N) into GaAsN grown under a hydrogen atmosphere was analyzed. GaAsN with small N content has the zinc blende structure, and in this system it is difficult for nitrogen (N) to be incorporated into the solid owing to the large difference in the bond lengths of Ga-N and Ga-As. Therefore, we first determined the stability of reconstructed GaAs(001) surfaces absorbed by hydrogen (H) in dependence on chemical potentials of the constituent elements, and we found that two hydrogenized structures appear when the partial pressure of hydrogen is high. Then energies needed for N substitution to the As site were calculated. The results suggest that N is more easily substituted to surface sites bonded with H, which could be the origin of H-related defects. We are planning to apply this approach to actual mineral system.

Keywords: First-principles calculation, growth surface, surface reconstruction

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Development of 3-D interferometer and refractive index matching cell for crystal growth

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It is known that the crystal growth mechanism in the solution changes as the supersaturation increases. When the crystal is growing in the supersaturating solution, the solute concentration at an interface between crystal and solution is smaller than that of the bulk solution because the crystal grows by incorporating solute in a solution. Since local concentration distribution at the interface can cause instability of the form on the crystal surface, determination of the concrete concentration distribution at the interface is important to discuss the mechanism of the crystal growth. Therefore, to discuss the relation between the crystal growth mechanism and growth rate of the crystal, it is necessary to measure the concentration around the crystal-liquid interface, not of the bulk.

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

To improve the disadvantage on the 2-D observation, a method of computer tomography (CT) has been adopted by some authors. By using the CT method, one 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). Previous works of 3-D observations revealed the 3-D structure of solute convection around the growing crystal. However, there are quite a few observations of the concentration field at the interface between crystal and solution..

In the present study, we carried out 3-D observation to measure the 3-D concentration field very close to the crystal-liquid interface growing in solution quantitatively. We newly developed microscopic Mach-Zehnder interferometer.

For quantitative 3-D measurement of concentration field, we developed a 3-D microscopic Mach-Zehnder interferometer. 3-D observations can provide us the concentration distribution at an interface between the growing crystal and solution with high magnification and high sensitivity.

For the application of the 3-D observation by using our Mach-Zehnder interferometer, we measured the concentration field around a protein crystal growing in a solution. The growth rate of the protein crystal is quite low, so the decrease of concentration in solution should be much smaller. The interference fringes obtained are straight, but curved slightly only at a very narrow area close to crystal surface. In spite of the very small movements of the interference fringes, we successfully reconstructed the 3-D concentration field around the growing protein crystal.

To use the 3-D observation of the concentration field at a rough interface or the interface in early stages of crystal growth, it is important to raise the spatial resolution of 3-D microscopic Mach-Zehnder interferometer further. The spatial resolution of the 3-D observation depends on the number of view angles. As the number of the view angles, namely the number of the images of 2-D concentration field, increases, resolution of reconstructed 3-D concentration field image gets better.

To get many 2-D images, we prepared cylindrical growth cell. Usually, cylindrical cell is not able to use for the interferometer because the curvature of the cell bends the light beam. We will overcome this problem by using the refractive index matching method.

To avoid bending of the light beam, we put the matching liquid around the cylindrical cell. This liquid removes refraction and reflection of the light on the wall of the cylindrical cell so that the beam can pass through the cell straightly.

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Step free energy of inorganic single crystal suraface

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Specific surface free energy of inorganic single crystal was experimentally determined by contact angle of liquid droplet on the crystal surface, and comopared with eth equilibrium grown length of each face. The relationship between specific surface free energy of the faces of the indivitual crystal with the same index and the equilibrium grown length of the face was linear. The difference of the specific surface free energy for the face of the same index can be explained by the differnce of step lengh on the crystal surface.

Keywords: crystal surface, crystal growth, free energy

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Nanoscopic Approach for Carbon Sequestration

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Growth mechanism of calcium carbonate crystals for carbon sequestration has been studied in-situ by FM-AFM, TEM and phase-shift interferometry, those of which have never been employed in this field. It was found that controlling polymorphs of calcium carbonate crystals is the key issue for the efficient sequestration.

Keywords: crystal growth, carbon sequestration, calcium carbonate