

高速原子間力顕微鏡によるカルサイト溶解過程の原子分解能観察

Atomic-Resolution Imaging of Calcite Dissolution Processes by High-Speed Atomic Force Microscopy

*福間 剛士¹*Takeshi Fukuma¹

1. 金沢大学

1. Kanazawa University

炭酸カルシウム鉱物は、地球規模の炭素循環において重要な役割を果たし、それにより地球の大気・水質・地質環境に大きな影響を及ぼす。なかでもカルサイトは、最も豊富に存在し、かつ、反応性に富むため、その結晶成長・溶解過程はとりわけ重要である。特に、最近では大気中の二酸化炭素濃度の上昇を抑制するために、地中への大規模かつ長期的な炭素貯蔵が検討されており、貯蔵された炭素の漏洩の原因となるカルサイトの結晶溶解過程は、大きな注目を集めている。このような長期的かつ大規模な炭素循環を正確に予測するためにも、カルサイト結晶の溶解機構を正確に知る必要がある。

これまでにも、カルサイトの溶解過程は様々な手法により研究されてきた。マクロな挙動については、溶解過程に伴う溶液中のイオン濃度変化を解析することで研究が進められてきた。ナノスケールの挙動については、原子間力顕微鏡 (AFM) や光学的な手法により、単原子ステップのフローを実空間観察することで、その溶解機構が研究されてきた。しかし、原子レベルの結晶溶解モデルを理解するためには、ステップ近傍の原子レベルの挙動を正確に知る必要がある。しかし、従来の分析手法ではこれを直接観察することが困難であったため、未確立の部分が残されている。

周波数変調原子間力顕微鏡 (FM-AFM) は従来超高真空中での原子・分子レベルの表面構造・物性計測に用いられてきた技術である。2005年に我々は、この顕微鏡を液中で動作させる技術を開発し、液中原子分解能観察を可能とした。さらに、近年、我々は液中FM-AFMの観察速度を、従来の~1 frame/minから~1 frame/secへと格段に向上させることに成功した。本研究では、この高速FM-AFMを用いて、カルサイトの溶解過程を直接原子分解能観察することに成功した。その結果、溶解途中の単原子ステップ近傍に、1-8 nm程度の幅を持つ遷移領域が存在することを発見した。この遷移領域の起源については、現在検討段階であるが、原子レベルの結晶溶解機構の理解を大きく進める発見であることは間違いない。このように、従来見ることのできなかつリアルタイムの構造変化を直接観察する技術により、今後、様々な結晶の成長・溶解過程に関する理解が進むものと期待される。

キーワード：原子間力顕微鏡、カルサイト、結晶溶解

Keywords: Atomic Force Microscopy, Calcite, Crystal Dissolution

固液界面の原子スケール観察によるモンモリロナイトのイオン交換に対する水和構造依存性の解明
Dependence of ion exchange on the hydration structure of montmorillonite surfaces probed
by atomic-scale observation of solid-liquid interface

*荒木 優希¹、佐藤 久夫²、大西 洋¹

*Yuki Araki¹, Hisao Satoh², Hiroshi Onishi¹

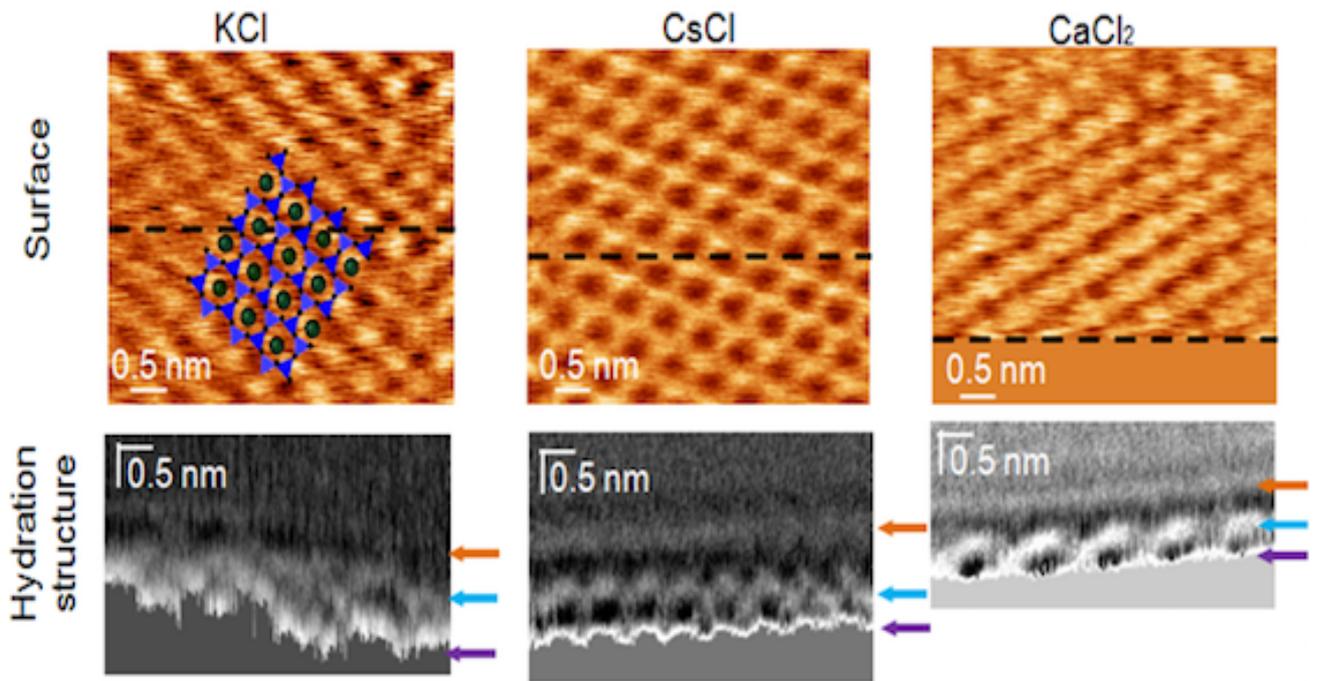
1.神戸大学大学院理学研究科、2.三菱マテリアル

1.Graduate School of Science, Kobe University, 2.Mitsubishi Materials Corporation

Cations of clay mineral are exchangeable depending on the atomic weight and electric density. Because of this ion exchange property, the clays are expected to capture the radionuclide which is diffused in the soil. Recently, the effect of water molecules on the ion exchange tendency has been suggested (S. Charles et al., 2006). In order to clarify the behavior of the water molecules at the clay-solution interface, we conducted the atomic-scale observation of the hydration structure in the vicinity of the montmorillonite surfaces in several ionic solutions. The frequency modulation atomic force microscopy (FM-AFM) which was modified based on the commercial AFM (SPM-9600, Shimadzu Corp., Japan) was employed for the atomic scale observation of interfacial structure (T. Fukuma et al., 2005). This FM-AFM technique has achieved the visualization of the 2D or 3D density map of the water molecules in the vicinity of crystal surfaces (K. Kimura et al., 2010; T. Fukuma et al., 2010). We observed the natural montmorillonite surfaces by FM-AFM in the 0.1 M KCl, CsCl, CaCl₂ solutions, respectively. The 100 nm plate-like particles of the montmorillonite were fixed on the mica substrate surfaces, then the (001) face and the interface were observed (Fig.1). The upper images in Fig.1 show the topography of the montmorillonite surfaces. The protrusions (brighter areas) indicate the cation sites of the montmorillonite surfaces which were located in the center of the six-membered rings of silicate tetrahedra. The interface of the montmorillonite and the solutions were observed along the dashed line in the upper images (bottom images in Fig.1). The bottom images showed the three brighter layers presented by arrows. These brighter areas indicate the distribution of the hydrated water molecules. Our results revealed that the hydration structure in the vicinity of the montmorillonite surfaces is uniform regardless of the cations in the solutions. It is suggested that the water molecules around the surface would not affect the ion exchange at the clay surfaces.

キーワード：粘土鉱物、イオン交換、水和、周波数変調方式原子間力顕微鏡

Keywords: clay mineral, ion exchange, hydration, frequency modulation AFM (FM-AFM)



Electron Backscatter Diffraction (EBSD)法による結晶方位同定のためのEuler角の検討
Euler angle calculation and evaluation for orientation indexing of Electron Backscatter
Diffraction(EBSD)

*森田 博文¹、Goulden Jenny²

*hirobumi morita¹, Jenny Goulden²

1. オックスフォードインストゥルメンツ株式会社、2. Oxford Instruments Nanoanalysis

1. Oxford Instruments KK, 2. Oxford Instruments Nanoanalysis

近年走査型電子顕微鏡(SEM)を用いた電子線散乱回折(Electron Backscatter Diffraction)－いわゆるSEM-EBSD法の地質学領域への応用が広がっているが、これまでの金属学の領域での応用の多くは立方晶での方位解析であった。しかし次第に金属・半導体・地質などのより広い領域や複雑な材料に広がるにつれて、六方晶や正方晶などの180度対称性の結晶への応用の必要性が高まってきている。EBSD法では菊池パターンから指数付けを行っているので、菊池パターンの対称性で識別できない方位に関しては方位を完全に決定することは難しい場合がある。さらに測定試料を70度に傾斜して測定するため、試料の傾斜方向、検出器との相対関係、SEMのスキャン方向などのパラメーターが最終的な方位決定のために重要な役割を果たしている。3次元の方位を示すEuler角の定義はBungeの表記法に則っていることが多くの場合測定の基準であるが^{[1][2][3]}、その表記法も測定系の座標によって異なる場合がある。今回は測定系の座標とEuler角の関係をまとめて各々の測定系での解釈の仕方を整理した。特に六方晶や正方晶などの対称性の低い結晶での方位の解釈を中心にして、90度対称性と180度対称性および360度対称性での結果の違いを試みている。

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キーワード：オイラー角、EBSD

Keywords: Euler angle, EBSD



Fig.1 detector to sample direction

透過型電子顕微鏡を用いたタンパク質の結晶化における準安定相の直接観察

Direct observation of metastable phase in protein crystallization using transmission electron microscopy

*山崎 智也¹、木村 勇気¹*Tomoya Yamazaki¹, Yuki Kimura¹

1.北海道大学低温科学研究所

1.Institute of Low Temperature Science Hokkaido University

A thermodynamically metastable phase, such as amorphous and dense liquid, has an important role in a crystallization process. In a nucleation process, amorphous particles appear before nucleation of a crystalline phase, and those serve as nucleation sites for more energetically favorable crystalline phases [1]. In crystal growth processes, a dense and liquid-like cluster most likely assists formation of a macro-step on a crystal surface [2]. To demonstrate these crystallization processes, *in situ* observation using a microscope is one of the powerful methods because it can directly visualize these processes in real time. However, it is difficult to visualize behavior of such metastable particles because those sizes are normally submicron, sometimes in nanoscale. Recently developed liquid cells adapting to high-vacuum environments of transmission electron microscopy (TEM) provide nanoscale views of nanoparticles and crystallization processes in aqueous solutions [3]. We developed the fluid-reaction transmission electron microscopy (FR-TEM) system for *in situ* observation of crystallization process in aqueous solutions. Using this system, we performed *in situ* observation of a protein crystallization, for investigating its nucleation and crystal growth processes.

Hen-egg white lysozyme was used as a protein sample without further purification and was crystallized using NaCl as a precipitant in a sodium acetate buffer solution at pH = 4.5. For observation of crystals in a solution under TEM, we used a "Poseidon" TEM holder (Protochip, Inc.) combined with a liquid cell. The liquid cell consists of a pair of semiconductor-based plates with an amorphous silicon nitride window and 150 or 500-nm-thick spacer to form a flow path of a crystallization solution.

We succeeded in observing two crystalline phases of orthorhombic and tetragonal in addition to an amorphous phase of the lysozyme [4]. Orthorhombic is the most stable of phases in our experimental solution. In this presentation, we present recent results of *in situ* TEM observation of its crystallization process including behaviors of metastable phases.

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キーワード："その場"観察、透過型電子顕微鏡、結晶化、溶液成長、リゾチーム

Keywords: In situ observation, Transmission electron microscopy, Crystallization, Solution growth, Lysozyme

塩素酸ナトリウム水溶液中の銀ナノ粒子円偏光光学捕捉により誘起されるキラル結晶化におけるキラリティの偏り

Chiral Bias in Chiral Crystallization Induced by Circularly Polarized Laser Trapping of Silver Nanoparticles in Sodium Chlorate Solution

*新家 寛正¹、杉山 輝樹²、田川 美穂³、村山 健太³、原田 俊太³、宇治原 徹³

*Hiromasa Niinomi¹, Teruki Sugiyama², Miho Tagawa³, Kenta Murayama³, Shunta Harada³, Toru Ujihara³

1.国立大学法人千葉大学融合科学研究科附属分子キラリティ研究センター、2.台湾国立交通大学応用化学系および分子科学研究所、3.国立大学法人名古屋大学未来材料・システム研究所未来エレクトロニクス集積研究センター

1.Molecular Chirality Research Center, Graduate School of Advanced Integration Science, 2.Applied Chemistry and Institute of Molecular Science, Taiwan National Chiao Tung University, 3.Institute of Materials and Systems for Sustainability, Graduate School of Engineering, Nagoya University

Chiral crystallization, in which chirality emerges spontaneously in the course of crystallization, has been received attention from the viewpoint of emergence of chirality. Thus, the exploration of physical factors that induce a chiral bias in chiral crystallization provides implications for the origin of bihomochirality. Asymmetric interaction between circularly polarized light (CPL) and chiral compound, i.e. circular dichroism (CD), has been considered as a candidate for the origin of bihomochirality,[1]. Many previous studies on photosynthesis of chiral molecule have proven that asymmetric light-matter interaction induces slight chiral bias in enantiomeric ratio of reaction product, so far.[2] However, light-based chiral bias in chiral crystallization still remains unreported. Two conceivable reasons may exist: (1) CD is intrinsically small, (2) there is no investigation on chiral bias by CPL-induced chiral crystallization with a guarantee of optical field effect on nucleation. We overcome these difficulties by two strategies: (1) the plasmonic enhancement of CD [3] and (2) continuous-wave (CW) laser-induced nucleation [4]. In this presentation, we report the first demonstration of significant chiral bias in NaClO₃ chiral crystallization by irradiating a tightly-focused circularly polarized CW laser at the interface between air and a NaClO₃ solution containing plasmonic AgNPs.

A CW CPL green laser (532 nm, 940±5 mW, ellipticity >93%) was focused onto the air-liquid interface of the undersaturated NaClO₃ solution containing AgNPs by using a 60x objective lens (NA = 0.9) equipped on an inverted polarized light microscope. We repeated crystallization and chirality identification of the NaClO₃ crystal 100 times and 100 times by using *l*- and *r*-CPL, respectively. The number of the resulting enantiomorphs was counted.

As the result of the laser irradiation, crystallization occurred from the focal spot. The crystallization using *l*-CPL(*r*-CPL) yielded *l*-enantiomorph 42(65) times and *d*-enantiomorph 58(35) times, respectively, indicating that the *d*-(*l*-)enantiomorph was dominant over the *l*-(*d*-)enantiomorph. Namely, the "dominant" enantiomorph can be switchable by switching the handedness of incident CPL, i.e. the chiral bias is enantioselective. In total, the "dominant" enantiomorph crystallized 123 times out of 200 crystallization. This chiral bias is statistically significant because the number of the "dominant" enantiomorph deviates 99% interval of the binomial distribution $B(n,p) = B(200,0.5)$, where n is the number of trials and p is the probability that the "dominant" enantiomorph crystallizes out (Figure 1). This deviation demonstrates that the probability p is more than 0.5, i.e. the probability of the occurrence of each enantiomorph is no longer equal.

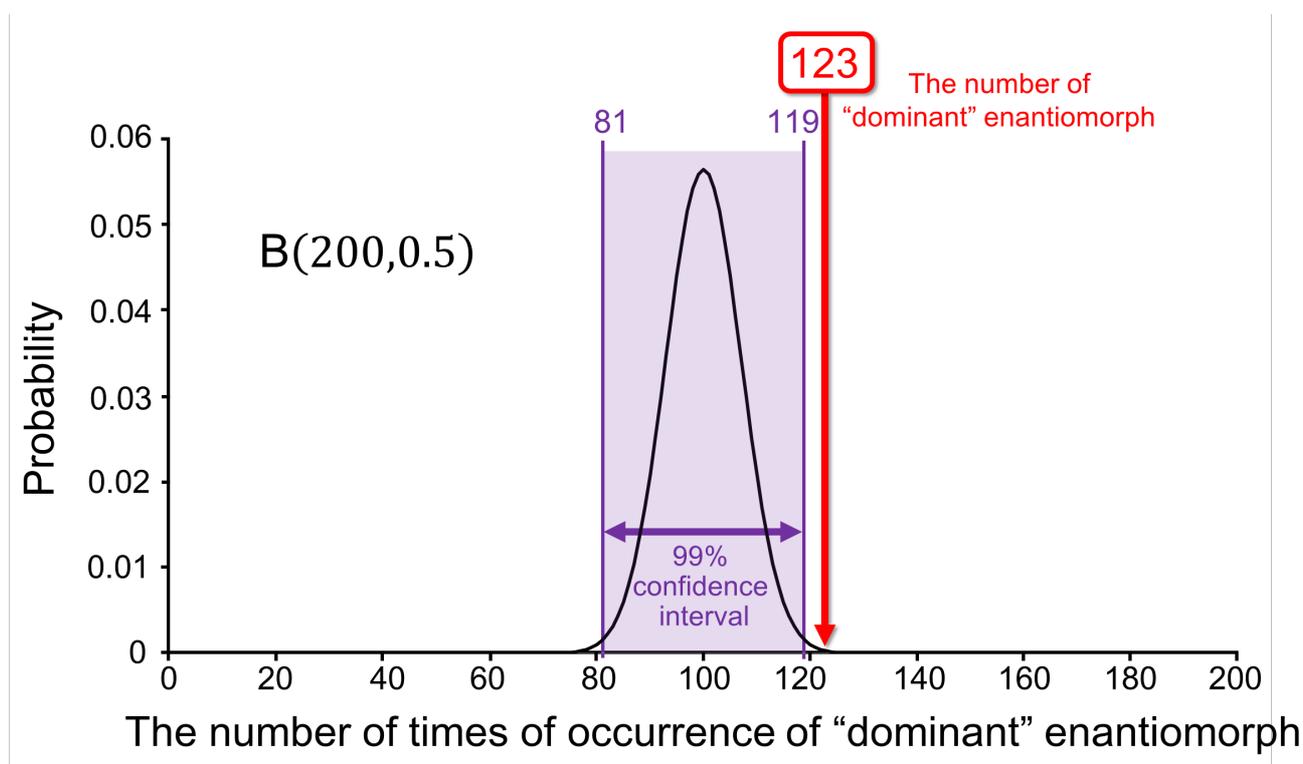
We found that the crystallization of NaClO₃ chiral crystal can be induced by the irradiation of tightly focused CPL laser (532 nm) at the interface between air and NaClO₃ solution containing

AgNPs. We also found that this crystallization method can cause a statistically-significant chiral bias in the probability of crystallization of both of the enantiomorphs. Moreover, the “dominant” enantiomorph is found to be switchable by changing the handedness of CPL. Our results may provide implications for the origin of bihomochirality.

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キーワード：キラル結晶化、レーザー誘起結晶化、円偏光、金属ナノ粒子、局在型表面プラズモン

Keywords: chiral crystallization, laser-induced crystallization, circularly polarized light, metal nanoparticle, localized surface plasmon



結晶の成長と溶解およびその形態

Formation of patterns in growth and dissolution of crystals

*横山 悦郎¹*Etsuro Yokoyama¹

1. 学習院大学計算機センター

1. Computer Centre Gakushuin University

This talk is concerned with fundamental aspects of formation of pattern of crystals in undersaturation. The formation of patterns in crystal growth is a free-boundary problem in which the interface that separates the crystal from an associated solution or vapor phase moves under the influence of non-equilibrium conditions. The formation of patterns in crystal dissolution/evaporation is also a free-boundary problem. The topics of dissolution/evaporation pattern of crystals, however, have been neglected in comparison with the study of growth morphology of crystals except a few studies [1].

The growth patterns depend markedly on conditions in the solution/vapor phase, such as temperature and concentration, which influence the growth speed of each element of the interface. The growth speed of the interface also depends on the local geometry of the interface, specifically on the interface curvature and the orientation of the interface relative to the crystal axes. Although the dissolution/evaporation forms diminish with time, the patterns could also depend on conditions in the solution/vapor phase under the small deviation from equilibrium conditions.

The local motions of interface can, in principle, be determined by solving the transport equations that take into account the following elementary processes:

- 1) a diffusion process for the transport of latent heat liberated or absorbed at the interface,
- 2) a process for diffusing molecules through the solution/vapor phase toward or from the interface, and
- 3) an interface kinetic process for incorporating/decorporation molecules into/from a crystalline phase at the interface[2].

We consider the asymmetry of normal speed at interface relative to the equilibrium point from supersaturation to undersaturation. We shall term the positive normal speed the growth rate of crystallization and the negative normal speed the dissolution/evaporation rate. Both local normal speed V of the interface can be proportional to the deviation from local equilibrium conditions Δ , which depend on interface curvature:

$$V = \beta \Delta,$$

where β is a kinetic coefficient that can depend on interface orientation and the degree of supersaturation or undersaturation at the interface. In general, V includes the Boltzmann factor $\exp(-E/kT)$, where E is an activation energy, k is the Boltzmann constant and T is temperature. Since the factor $\exp(-E/kT)$ causes enhancement of the dissolution/evaporation rate for $T > T_e$ but reduction of the growth rate for $T < T_e$, the behavior of V relative to T_e is asymmetric. On the other hand if V is controlled by the undersaturation and the factor $\exp(-E/kT)$ does not work, the dissolution rate can approach a limiting value. This is because the degree of undersaturation has a minimum limit, e.g., pure solvent without solute.

In this talk, we show the patterns during growth or dissolution/evaporation of a two-dimensional crystal under conditions such that the transport of heat and/or solute is so rapid that growth is controlled by interfacial processes. Furthermore, we discuss the formation of both patterns in the point of view of the asymmetry of normal speed at interface relative to the equilibrium point.

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結晶の成長と溶解の複合

The Coupled Dissolution and Growth

*塚本 勝男¹*Katsuo Tsukamoto¹

1.大阪大学大学院工学研究科

1.Graduate School of Engineering, Osaka University

Lots of discussions on whether growth is an opposite phenomena of dissolution or not. Here after presenting the real rates observed in-situ in both cases at the same absolute value of chemical potential, we show the difference. This may lead to a deeper understanding of coupled dissolution and growth of crystals in solution. We will show even in dissolution process of a crystal crystallization barrier plays an important role.

キーワード：溶解、結晶成長、メカニズム

Keywords: dissolution, growth, mechansim

NaCl単結晶の表面自由エネルギー密度とラフニング転移

Specific Surface Free Energy and Roughening Transition of Sodium Chloride Single Crystal

*丸山 諒也¹、鈴木 孝臣¹*Ryoya Maruyama¹, Takaomi Suzuki¹

1.信州大学大学院総合理工学研究科

1.Graduate School of Science and Engineering, Shinshu University

Specific surface free energy (SSFE) is one of important values to discuss the morphology and growth of crystal, and theoretically well discussed. However, experimental trial to determine the SSFE of crystal is very few. We have already measured contact angle of liquids on crystals, for example, apatite, ruby, and quartz in order to determine the SSFE. The SSFE of crystals were proportional to growth rate of crystals, which qualitatively satisfy Wulff's relationship. Experimentally determined SSFE is not that of ideal flat face, but it includes step free energy. This time we tried to measure the step free energy of sodium chloride and discussed the roughness of crystal face.

Sodium chloride single crystal was synthesized by evaporation of saturated water solvent keeping at 40°C. Cubic crystal with (100) face was obtained. Octahedral sodium chloride single crystal with (111) face was also synthesized from water solvent with 15% of formamide keeping also at 40 °C. Crystals was heated by electric furnace at 600°C and kept for 1 hour.

Droplets of ethylene glycol or diethylene glycol with volume of 0.1μL were dropped on the crystal surface using a micropipette. The contact angle were observed using digital camera.

SSFE were calculated by Wu's harmonic mean equation and Fowkes approximation. The calculated value of SSFE of (100) surface before and after heat treatment were 45.9, 48.8mN/m, and SSFE of (111) face before and after heat treatment were 37.9 and 38.9mN/m. The SSFE was increased by heat treatment for (100) and (111) face. Because the observed SSFE contains step free energy, the increase of SSFE is caused by increase of steps on the crystal face. The increase of SSFE was observed after the heat treatment at 600°C. Therefore, the roughening temperature is considered to exist at the temperature under 600°C.

キーワード：表面自由エネルギー密度、NaCl単結晶、ラフニング転移

Keywords: specific surface free energy, sodium chloride single crystal, roughening transition

液相からの気泡核生成の大規模分子動力学計算による気泡表面張力の算出

Surface energy of bubbles evaluated by large-scale molecular dynamics simulations of homogeneous bubble nucleation

*田中 今日子¹、田中 秀和²、アンジェリル レイモンド³、ユルグ ディアモンド³*Kyoko Tanaka¹, Hidekazu Tanaka², Angelil Raymond³, Juerg Diemand³

1.北海道大学低温科学研究所、2.東北大学、3.チューリッヒ大学

1.Institute of Low Temperature Science, Hokkaido University, 2.Tohoku University, 3.Univ. of Zurich

液体からの気泡生成は様々な分野に関わる重要な現象のひとつであるが、その気泡の核生成過程についての理解は未だ限られている。古典的核形成理論は、核形成過程の巨視的記述を与え広く用いられているが、理論から得られる核生成率は実験や分子動力学(MD)シミュレーションからの得られる核生成率と大きくずれることが指摘されている。例えば、従来のMD計算から得られた気泡の生成率は古典的理論と比較すると、ほとんどの場合において古典的理論の核生成率よりも3桁から20桁程度も高くなる結果が得られているが、その原因は未だ明らかではない [1]。我々は LAMMPS を用いて 5 億体のレナードジョーンズ(LJ)分子から成る液相からの気泡核生成の分子動力学(MD)計算を行った。温度は $T/(\epsilon/k) = T^* = 0.6 - 0.86$ (ϵ はLJ系のエネルギー単位, k はボルツマン係数)、圧力 P は $-300 < P/P_{eq} < 0.5$ (P_{eq} は平衡蒸気圧)のさまざまな範囲において、NVE系のもとで気泡が生成し成長する様子を観察した。従来のMD計算の多くは初めの気泡が形成される時間から核生成率を見積もる MFPT 法(the mean first passagetimes)が用いられてきたが、本研究では複数の気泡の発生から核生成率を求める方法(Yasuoka-Matsumoto method)を用いて正確に核生成率を求めることに成功した。また気泡のサイズ分布から気泡生成のための自由エネルギーの算出や気泡の物理的性質など詳細な解析を行った

[1,2]。我々が得た核生成率は、古典的理論から得た値と高温で一致する一方、低温では大きくずれ、理論値より大きくなる。この古典的理論とのずれは以下のように説明される。従来の理論では核生成率 J の表式は $J = J_0 \exp(-G/kT)$ であり、プレファクター J_0 は液体圧力に依らない一定の値とされてきた(但し、 G は核生成の自由エネルギー)。しかし一方で、 J_0 は臨界核付近での気泡の成長率により決定し、液体圧力に大きく依存することが指摘されている[3]。とくに液体圧力と平衡圧力の差が十分大きい場合には、気泡の周りの流体の慣性や粘性が効き、上記のプレファクターと数桁異なる[4]。正確なプレファクターを用いて得られた核生成理論とMD計算を比較することによりナノサイズの気泡の表面張力を算出できる。これら2つの古典的理論の改良により多くのMD計算や実験が説明可能である。

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微小重力下におけるアルミナの均一核生成過程の赤外スペクトルその場測定

In-situ IR measurement in homogeneous nucleation process of alumina under μG environment*石塚 紳之介¹、木村 勇気¹、山崎 智也¹、左近 樹²、稲富 裕光³*Shinnosuke Ishizuka¹, Yuki Kimura¹, Tomoya Yamazaki¹, Itsuki Sakon², Yuko Inatomi³

1.北海道大学低温科学研究所、2.東京大学大学院理学研究科、3.宇宙航空研究開発機構

1.Institute of Low Temperature Science, Hokkaido University, 2.Graduate School of Science, University of Tokyo, 3.Japan Aerospace Exploration Agency

Homogeneous nucleation process from vapor is characterized by the ratio between time scales for supersaturation increase and for source collision expressed as Λ [1]. Under the physical condition with the same Λ value, homogeneous nucleation process has been regarded to follow the same process. At the dust forming front around evolved stars, Λ value has been calculated to be $\sim 10^{3-5}$ from total pressure and velocity of stellar wind. In contrast, Λ value of $\sim 10^{0-2}$ is known for the gas evaporation method which is one of the simplest experimental methods to produce dust analogues via homogeneous nucleation [2, 3].

In-situ IR measurement during nucleation of nanoparticles in the gas evaporation method proved multi-step formation of metal oxide from vapor to crystalline via liquid droplet in our ground based experiment [4]. Using our advanced technique, we measured IR spectra of nucleating alumina and its evolution while nanoparticles are free-flying under μG environment in which Λ approximates to the value at dust formation region. Specially designed experimental apparatus equipped with dispersive IR spectrometer was loaded to S-520-30 sounding rocket by which the apparatus carried to altitude of 312 km. We also performed ground based experiment combined with FT-IR.

IR spectra of nucleating alumina measured in ground based experiment showed broad absorption extending $>11 \mu\text{m}$. Formed nanoparticles were observed by TEM and identified to δ -alumina. In contrast, sharp absorption centered at $13 \mu\text{m}$ was appeared in μG experiment. This $13 \mu\text{m}$ band is one of the most indicative features of corundum (α -alumina) sphere. Corundum is the most plausible candidate for the origin of unidentified $13 \mu\text{m}$ feature which is often observed for oxygen rich AGB stars with low-mass loss rate [5, 6]. Polymorphic behavior of alumina in homogeneous nucleation process at different Λ will be the key to understand astronomical dust formation.

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