MIS31-01　　　　　　　会場:102A　　　　　　　　　　　時間:5 月 27 日 09:00-09:30

ガスハイドレート溶解時のナノバブル生成と再結晶化過程におけるメモリー効果
Nanobubble formation in gas hydrate dissolution process and memory effect of gas hydrate recrystallization

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Gas hydrate is the ice-like crystal formed by water molecules (host lattice) and gas molecules (guests in the cages). Usually the initial nucleation of gas hydrate requires the large super saturation (or super cooling) conditions. However, the recrystallization from the solution dissociated the gas hydrate crystal requires the smaller super saturation compared to the initial one. This phenomenon is called 'memory effect' of gas hydrate formation, which is expected to be used for the industrial utilization of gas hydrates.

The mechanism of the memory effect has not been revealed yet, but several models have been proposed. One of them is considered that the cage-like structure is remaining in the dissolved solution even after the crystal dissociation. We consider that, in addition to the host lattice formation, the condensation process of guest molecules would be required for the recrystallization of gas hydrates. It is because the guest molecule concentration in the crystal is much higher than the solubility in water. As one of the possible idea of this gas condensation process, we consider that the nanobubbles would be formed when the gas hydrate is dissolved. In the gas hydrate crystal, each guest molecule is encaged in the cage. When the gas hydrate crystal is dissolved in the solution, guest molecule would be dissolved in the solution one-by-one. Thus the gas molecule aggregation formed in the solution would be small, that is, becomes nanobubble.

The Nanobubble has several unique properties and been expected to apply to various industrial utilizations. The size of bubble is so small that the nanobubble can be existed in the solution without floatation. Also the internal pressure of bubble is considered to be very large, a large amount of guest molecules is expected to exist in the area of dissociation although the bubble is too small to be observed by an optical microscope. In the present study, we aim to confirm the existence of nanobubbles in the solution after the gas hydrate dissolution. We used the transmission electron microscope to observe the nanobubbles by using the freeze-fracture replica technique.

キーワード: ナノバブル, ガスハイドレート, メモリー効果, 凍結割断レプリカ法, 透過型電子顕微鏡
Keywords: nanobubble, gas hydrate, memory effect, freeze-fracture replica technique, transmission electron microscope

MIS31-02　　　　　　　会場:102A　　　　　　　　時間:5 月 27 日 09:30-09:45

塩素酸ナトリウムナノ結晶の溶解過程の TEM 観察
TEM observation of dissolution process of sodium chlorate nanocrystals

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Recent years, we are focusing on nanometer scale live imaging of nucleation and dissolution of crystals in a solution using transmission electron microscope (TEM) to know the fundamental processes. Since, basically, high-vacuum environment has to be maintained in the TEM during the observation, sample is limited. To overcome the difficulties to introduce a solution into a TEM, very ingenious graphene cell or specially designed amorphous silicon nitride membrane has been established and achieved in situ observation of nucleation [e.g., 1-4]. As the results, several new perspectives such as, non-classical nucleation pathway, coalescence and oriented attachment, in the nucleation process have been reported. Against the use of liquid cell, we used ionic liquid as a solvent instead of water to avoid evaporation of a solvent in the high-vacuum of a TEM [5]. Ionic liquids have a great properties for TEM observation, such as negligible vapor pressure and high electrical conductivity. As the result, following new consequences were found after experiments of sodium chlorate nanocrystals.
1. Solubility-independent formation of polymorph.
2. Crystals do not dissolve smoothly but in a fluctuating manner.
3. New crystals form even in a totally dissolving system.
4. Ripening occurs but different from Ostwald ripening.
In case of Ostwald ripening, initially presenting larger particles grow as a result of dissolution of smaller particles. However, our observation shows that ripening occurs with accompanying formation of new crystals, i.e., most of the initial crystals is replaced by new crystals. In the presentation, we will show the difference of the dissolution process between in ionic liquid and water solutions, which can be observed by a special holder having a liquid cell for TEM observation.

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キーワード: 透過電子顕微鏡, 溶解, ナノ, その場観察
Keywords: TEM, dissolution, nano, in-situ observation

圧密されたスメクタイト粘土の溶解挙動
Dissolution behavior of compacted smectite clay

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　天然ベントナイトを構成する粘土鉱物であるスメクタイトは、隕石から堆積岩まで広く存在するミクロン─ナノ結晶である。スメクタイトはその成長後の {001} 積層状態から膨潤後のランダム積層状態まで様々な形態を持つことができるため、溶解挙動については不明な点が多い。例えば、コロイドとして分散状態にあるスメクタイトは pH と未飽和 ΔG、温度に駆動されて (Sato et al., 2005) 速く溶解するが、圧縮した場合の溶解速度は極めて遅くなり (Nakayama et al., 2013), 一種の安定状態になると思われる。

　スメクタイトの溶解挙動について、単分散状態の粒子を観察する AFM 測定は有効な手法であるが、高密度の圧密粒子における直接的な測定ができない。そこで垂直走査干渉計 (VSI) と自動圧縮セルを駆使したその場観察手法と、原子間力顕微鏡 (AFM) による粒子解析を融合した手法を開発した。この手法によって、アルカリ溶液 (0.3M NaOH) を通水しながら、70 ℃の高温で様々な密度に圧縮したスメクタイト (Na-montmorillonite) の圧密体を再現して、その場における物質体積の減少を連続測定した。また測定後の粒子はセルから回収して AFM によって単分子粒子の形状測定を行い、溶解過程の粒子のステップエッジ表面積の解析を行った。

　AFM-VSI 測定の結果、スメクタイトの溶解は、単分散の低密度ゲル (0.001 g/cm^3) から高密度状態 (1.64 g/cm^3) において、2.9E-11 から 2.6E-13 mol/m^2/s までの 2 桁減速していることがわかった。この原因としては、ナノ積層体であるスメクタイト粒子がお互いのステップエッジをマスクし合う自己マスキング効果が考えられる（溶解速度の減速）。しかしながら、ランダム積層状態での圧縮は、刃状転位の生成を促進し新たな溶解フロントを作り出すため、粒子の分割、すなわちステップエッジ面積の増大（溶解速度の加速）も圧縮初期には起きていることもわかった。

　このように高密度の粘土などのナノ積層体粒子には、圧縮によって初期には溶解の加速が起こるが、すぐに減速する負のフィードバック機構も備わっている。このような複雑な挙動を解明・理解するにはモンテカルロ計算などのモデリング手法が今後必要である。

キーワード: スメクタイト, 溶解, 圧密, AFM, VSI
Keywords: smectite, dissolution, compaction, AFM, VSI

MIS31-04　　　　　　　会場:102A　　　　　　　　　　　時間:5 月 27 日 10:00-10:15

モンモリロナイト表面におけるカチオン交換の原子スケールその場観察
Atomic scale in situ observation of cation exchange on montmorillonite surface

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　粘土鉱物はイオン交換性を有するため, 環境相に暴露した放射性核種の吸着材として核廃棄物処分技術への活用が期待されている。イオン交換に関する化学量論的な研究が数多く行われている一方, 粘土表面の微視的構造に対するイオン交換の選択性や, 吸着イオンの表面拡散など, 界面でのダイナミクスに関してはまだ明らかになっていない。本研究では, 固液界面の原子スケールその場観察の強力なツールである周波数変調方式原子間力顕微鏡 (FM-AFM) を用いて, モンモリロナイトを例に, その表面のイオン交換過程をその場観察した。モンモリロナイトは {001} 面が発達した約 100 nm のサイズの板状結晶であり, その表面にはナトリウム, カルシウムイオンが配位している。0.1 ～ 1 M の塩化セシウム溶液中で {001} 面の観察を行い, 結晶表面の格子点の凹凸の変化からイオン交換の可視化を試みた。発表では, セシウムイオンとの交換によるモンモリロナイトの表面トポグラフの変化を観察した結果を紹介する。

キーワード: 粘土, モンモリロナイト, イオン交換, 周波数変調方式原子間力顕微鏡
Keywords: clay, montmorillonite, ion exchange, frequency modulation AFM

MIS31-05 会場:102A 時間:5 月 27 日 10:15-10:30

蛍石およびアパタイトの表面自由エネルギー
Surface Free Energy of Fluorite and Apatite Crystals

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Specific surface free energy (SSFE) is significant value to explain the morphology of crystal. The relationship between SSFE and growth length of crystal face is considered to be proportional, which is known as Wulff's relationship, and well accepted for thermodynamic interpretation of crystal growth theoretically. Though Wulff's relationship is well accepted for theoretical analysis, experimental measurement of SSFE for crystal face is very few. According to Young's equation, SSFE of solid face can be introduced from contact angle of liquid on the solid face, and we observed SSFE of some crystals, for example, apatite[1], ruby[2], and quartz[3]. However, the SSFEs of crystal face have wide distribution even for a flat face of the crystal. Such wide distribution of observed SSFE was considered to result from steps on the crystal face. In this work, we observed SSFE of natural fluorite crystal. Natural fluorite crystal was cut and polished for (100), (110), and (111) faces. SSFE can be separated to dispersion component which results from van der Waals force and polar components which results from interaction between permanent dipole moments. The polar component of SSFEs on (100) and (111) faces were smaller then have large rate of dispersion component of than that on (110) face, because (100) and (111) faces are polarized face. Although the SSFE of real crystal is calculated from macroscopic value such as contact angles of liquid droplets, the SSFE reflects microscopic surface structure such as steps and the ionic morphology of the crystal face. We also observed SSFEs of apatite and fluorite crystals in order to demonstrate the effect of steps on the SSFE. Contact angle of water and formamide droplet on crystal face was observed using digital camera. SSFE was calculated using Fowkes approximation and Wu's harmonic mean equations. Though the crystals we experimentally obtained were growth form, the relationship between SSFE and the growth rate was almost proportional, which looks to satisfy Wulff's relationship qualitatively.

キーワード: 表面自由エネルギー, アパタイト, 蛍石
Keywords: Surface free energy, apatite, fluorite

MIS31-06　　　　　　　会場:102A　　　　　　　　　時間:5 月 27 日 10:30-10:45

ステップ・ダイナミクスの数値計算：フェーズフィールド法に基づいた定量的定式化
Numerical simulation of step dynamics: Quantitative formulation based on a phase-field method

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　ステップ・ダイナミクスは，結晶成長における本質的な物理現象である。結晶表面には原子スケールの高さを持つ段差（ステップ）が存在し，そこに原子や分子が取り込まれることによってステップが前進し，結晶が一層ずつ積み上げられていく。従って，結晶成長メカニズムを解明するには，ステップの供給メカニズムや，ステップ前進速度を決める物理を理解する必要がある。

　代表的なステップ供給メカニズムとして，1949 年にらせん成長機構が提案された [1]。結晶内に含まれるらせん転位が平坦な結晶表面に露出していると，そこを中心としてステップが渦巻き状に前進する。らせん転位は常にその表面に露出し続けるため，永続的なステップ供給源として作用し，転位露出位置を頂上とした成長丘を形成する。らせん成長機構による面成長速度は過飽和度の関数として解析的に表されており，成長に寄与するらせん転位の数や間隔，Burgers ベクトルの総和に依存する [2,3]。成長丘の傾きの過飽和度依存性かららせん転位源の特徴を決定することも可能である [4,5]。しかし，この解析式では，個々のステップの挙動を記述することはできない。実際の結晶成長においては，逆向きのらせん転位ペアの間に閉じたループ状ステップが形成されたり，二次元核形成によってステップ間に新たなステップが供給されたりすることがある [6]。個々のステップの挙動が結晶成長に及ぼす影響を明らかにするには，多数のステップのダイナミクスを同時に扱う手法が重要である。

　本研究では，フェーズフィールド法（PF 法）に基づき，多数のステップのダイナミクスを定量的に扱うことが可能な数値計算手法を提案した。PF 法は，多数のステップの相互作用を同一のスキームで扱うことが可能な数値計算手法である [7]。PF 法では，結晶面の高さをフェーズと呼ばれる秩序変数で表現する。フェーズはステップ間（テラス）において一定の値を取り，ステップにおいて異なる高さのテラスの間を有限の幅の間で連続的に繋ぐ。本研究では，過飽和度を陽に取り入れた自由エネルギー汎関数を新たに定義し，自由エネルギー減少の原理からフェーズ場の時間発展方程式（PF 方程式）を導出した。さらに，過飽和度が小さい極限において，直線状ステップの前進速度が direct integration 仮説 [3] によって決まる値（厳密解）に一致するように定式化した。本手法を代表的なステップ・ダイナミクスの問題に対して適用し，面成長速度の計算結果を解析式 [2,3] と比較した。

　まず，直線状ステップの前進速度の数値計算を行ない，厳密解との誤差が 1%以内になる計算条件を明らかにした。次に，過飽和溶液中における二次元島の成長・溶解過程の数値計算を行ない，半径の時間変化が Gibbs-Thomson 効果から予想される式と一致することを確認した。これは，本手法が曲がったステップの前進速度をも正しく記述できることを示している。さらに，シート構造関数 [7] を用いてらせん転位を導入し，らせん成長機構による面成長速度を調べた。その結果，らせん転位がひとつの場合，らせん転位がペアで存在する場合，同じ Burgers ベクトルを持つ複数のらせん転位が等間隔で一列に並んでいる場合のそれぞれについて，解析式 [2,3] を定量的に再現できることを示した。

　本研究では，複雑ならせん転位源に対してステップ・ダイナミクスを数値的に解く手法を提案した。本手法では，PF 方程式（放物型偏微分方程式）を一般的な数値計算法で解くことで，ステップ前進速度を曲率効果も含めて定量的に再現することができる。本手法は，ステップ・ダイナミクスの新たな解析手法を提供するだろう。

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キーワード: 結晶成長, ステップ・ダイナミクス, 数値計算, フェーズフィールド法
Keywords: Crystal growth, Step dynamics, Numerical simulation, Phase field method

MIS31-07 　　　　　　会場:102A 　　　　　　　　　時間:5 月 27 日 11:00-11:15

表面構造により制御される固体ベンゼンの水素原子トンネル付加反応
Controlling surface tunneling reactions of solid benzene via surface structure

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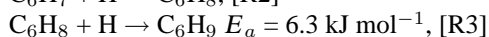HAMA, Tetsuya[1*] ; UETA, Hirokazu[1] ; KOUCHI, Akira[1] ; WATANABE, Naoki[1] ; TACHIKAWA, Hiroto[2]

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Organic molecular solids including thin films and fine particles generally exhibit a range of crystalline phases as well as an amorphous state. The dependence of chemical reactivities on their surface structure has attracted considerable attention because they play a crucial role in an almost limitless amount of research fields, ranging from atmospheric and interstellar chemistry to biological and material sciences. However, despite the rapid accumulation of structural information about organic materials, the correlation between the surface structure of these materials and their chemical properties is not fully understood. Here, we demonstrate that the surface structure of an organic molecular solid determines its chemical reactivity toward an adsorbate. We investigated the following sequential hydrogen (H) atom addition to amorphous and crystalline benzene (C_6H_6)

$C_6H_6 + H \rightarrow C_6H_7$ E_a = 18.2 kJ mol^{-1}, [R1]
$C_6H_7 + H \rightarrow C_6H_8$, [R2]
$C_6H_8 + H \rightarrow C_6H_9$ E_a = 6.3 kJ mol^{-1}, [R3]
$C_6H_9 + H \rightarrow C_6H_{10}$, [R4]
$C_6H_{10} + H \rightarrow C_6H_{11}$ E_a = 10.5 kJ mol^{-1}, [R5]
$C_6H_{11} + H \rightarrow C_6H_{12}$. [R6]
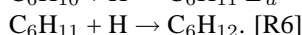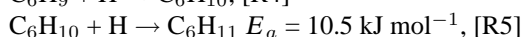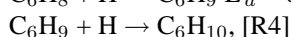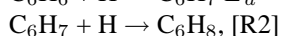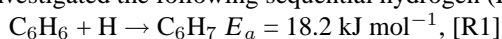
E_a is the activation barrier for H-atom addition in the gas phase. The radical recombination reactions R2, R4, and R6 are barrierless on the surface. In situ infrared spectroscopy revealed that cold H atoms can add to the amorphous benzene surface at 20 K to form cyclohexane (C_6H_{12}) by tunneling. However, hydrogenation of crystalline benzene is greatly suppressed. We suggest that the origin of the high selectivity of hydrogenation by tunneling is the difference of geometric constraints; that is, the presence of reactive dangling C_6H_6 molecules that lacks near neighbors on the amorphous C_6H_6 surface and the strong intermolecular steric hindrance on the crystalline C_6H_6. The present findings can lead us to a better understanding of heterogeneous reaction systems involving tunneling, and also provide the possibility of nonenergetic surface chemical modification without undesired side reactions or physical processes.

キーワード: 芳香族炭化水素, 水素化, アモルファス構造, 結晶構造, 量子トンネル効果, 反応制御
Keywords: Aromatic hydrocarbons, hydrogenation, amorphous structure, crystalline structure, quantum tunneling, reaction control

MIS31-08　　　　　　　会場:102A　　　　　　　　　　　時間:5 月 27 日 11:15-11:30

水蒸気から液滴への均質核生成の大規模分子動力学計算
Large molecular dynamics simulations of the vapor-to-liquid nucleation of water

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Phase transitions play important roles in many areas of science and technology. The classical nucleation theory (CNT) is the most widely used model for describing homogeneous nucleation and provides the nucleation rate as a function of the supersaturation ratio and the surface tension of a condensed phase. However, many studies have reported that the CNT fails to describe experimentally obtained results. In the case of water, the deviations between the nucleation rates predicted by the classical nucleation theory and the experimental values are several order of magnitude.

Molecular dynamics (MD) simulations are able to directly resolve details of the nucleation process, and provide useful test cases for nucleation models. Until now, many MD simulations examining the nucleation process of water molecules have been carried out [1-3]. Tanaka et al. [3] performed MD simulations of the nucleation of water vapor in order to test nucleation theories with 4000 water molecules. The results showed that the classical nucleation theory (CNT) and the modified classical nucleation theory (MCNT) overestimate the nucleation rates in all cases. On the other hand, the semi-phenomenological model, which corrects the CNT prediction using the second virial coefficient of a vapor, reproduced the formation free energy of a cluster within 10% and the nucleation rate J within one order of magnitude. The sticking probability of the vapor molecules to the clusters was also determined from the growth rates of the clusters. The sticking probability rapidly increases with the supersaturation ratio S, which is similar to the Lennard-Jones system. For such low-S cases, we must estimate the sticking probability precisely for the evaluation of J.

Previous typical MD simulations of homogeneous nucleation use 10^3-10^4 atoms. At low vapor densities, and therefore low supersaturations, a single nucleation event becomes unlikely to occur within reasonable computational timeframes. Simulations with larger number of molecules allow for the occurrence of such rare nucleation events, and enable us to measure these low rates. Recently, we started the large-scale MD simulations the SPC/E rigid water model with LAMMPS. In the simulations, the particle numbers are 1 to 120 million atoms (324000-4116000 molecules). We assumed NVT (constant volume and temperature) ensembles and used a three-dimensional periodic boundary condition with different parameters of temperature T and initial supersaturation ratio S. Here, first results for the water are presented. We obtained the smaller nucleation rates by 4 order of magnutude than the previous studies.

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キーワード: 核生成, 気相ー液相, 相変化, 分子動力学計算, 水
Keywords: nucleation, vapor to liquid transition, molecular dynamics simulation, water

高過飽和気相からの均一核生成過程の赤外スペクトルその場測定実験
Homogeneous Nucleation of Nanoparticles from Supersaturated Vapor Investigated by In-situ IR Measurement Experiment

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When we evaporate experimental materials in the atmosphere, nanoparticles condense from highly supersaturated vapor via homogeneous nucleation. This technique is known as the Gas Evaporation method. Nuclei must overcome energetic disadvantage of surface by making chemical bonds to form particles. Since energetic barrier for homogeneous nucleation is excessively high, homogeneous nucleation occurs from highly supersaturated vapor [1-3]. In such conditions, precursors should grow following kinetically feasible reaction path, which is deviated from equilibrium condensation. Furthermore, the size of nuclei is so small that they show quite different physical and chemical properties from that of bulk material. Therefore, chemical reaction processes and its properties during transition state of homogenous nucleation are still unrevealed.

For the purpose of examination of condensation sequences of nanoparticles, we investigated by a new experimental apparatus named Free-flying *In-situ* infrared measurement of Nucleating nanoparticles Experimental (FINE) system [4]. FINE system is for gas evaporation method combined with FT-IR and enables direct *in-situ* IR measurement of condensation of 10-100 nm nanoparticles via homogeneous nucleation from vapor.

We applied FINE system for silicate and titanium oxides and revealed that condensation proceeds through metastable phases with non-crystalline IR feature, which is known as Ostwald's step rule. Just condensed nanoparticles would be liquid droplet and crystallization proceeded subsequently. In previous study, we succeed in measurement of IR evolution after nucleation. However, the information about precursors is still lack to understand condensation mechanism. We are now developing a new experimental set up for FINE system and going to talk about future work.

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Keywords: Homogeneous Nucleation, Vapor Growth, in-situ, Nanoparticles

MIS31-10 会場:102A 時間:5 月 27 日 11:45-12:00

溶液中の結晶化過程の研究に対する透過型電子顕微鏡の応用
Application of the transmission electron microscopy to the study of the crystallization process in a solution

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One of the powerful methods to demonstrate the crystal growth and dissolution processes is in situ observation using a microscope, because it can directly visualize these processes in real time. The crystal growth and dissolution processes in a solution have been studied mainly using various optical microscopies as a noninvasive technique. Some high resolution optical microscopies is able to visualize the molecular-level structure on a crystal surface [1-3]. However, the lateral resolution of optical microscopy is sub-micron because it is limited by the wavelength of a light source [1]. To resolve the crystallization processes more clearly, the transmission electron microscopy (TEM), which has the nano-order resolution, is a strong method for in situ observation. Recently, in situ observations of the crystallization processes in solutions under TEM have been energetically performed using the liquid cells or an ionic liquid to adapt to the high-vacuum environment [4-6]. These observations allow us to see the behavior of nano-particles and crystallization process of inorganic materials in a solution. Here, using the liquid cell, we have performed in situ observation of the crystallization of a lysozyme protein, which is used to study the crystallization process in a solution as a model material, by the TEM for understanding the processes of crystallization.

We used two TEMs with LaB6 filament at an acceleration voltage of 200 kV (Hitachi H-8100) and with field-emission gun at an acceleration voltage of 300 kV (Hitachi HF-3300). For the observation of crystals in a solution, 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 the flow path of the crystallization solution. The lysozyme was crystallized using NaCl as a precipitant in a sodium acetate buffer solution at pH = 4.5.

As a result, we succeeded in observing the crystals and amorphous particles of lysozyme protein using the TEM and the liquid cell holder. In this presentation, we report the recent results of in situ observation of its crystallization process including the growth and dissolution.

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Keywords: in situ observation, transmission electron microscopy, crystallization, solution growth, lysozyme

MIS31-11   会場:102A   時間:5 月 27 日 12:00-12:30

ゲル中で成長したタンパク質結晶の成長と溶解
Growth and dissolution of the hydrogel-grown lysozyme crystals

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We recently developed a new method for growing protein crystals in a high-concentration hydrogel. Using the method we can crystallize protein crystals with increased mechanical stability, as a result the crystals give us high resolution of X-ray diffraction pattern. On the other hand the crystals contain the hydrgel fragments and the effects on crystal defects such as dislocations were unknown. In this study, we slightly etched the crystal surface and estimated the dislocation density.

Hydrogel-grown and solution-grown LZM crystals were slightly dissolved by increasing the temperature, and their surface morphologies were observed by laser confocal microscopy. The solution-grown crystals exhibited deep etch pits at 303 K, while the hydrogel-grown crystals exhibited etch pits at a higher temperature (305 K). In addition, the density of the etch pits on the solutiongrown crystals at 305 K was significantly higher than that on the hydrogel-grown crystals at the same temperature. These results demonstrate that the hydrogel-grown crystals are more tolerant of temperature changes than those grown in solution.