for $LuBO_3$ in process of annealing of the amorphous precursors: high vaterite phase → calcite phase ↔ high vaterite phase again instead of the previously known sequence: calcite phase ↔ high vaterite phase. For $LaBO_3$ instead of sequence: aragonite phase ↔ monoclinic phase in micro dispersed powders we have the sequence: monoclinic phase → aragonite phase ↔ monoclinic phase if the crystallization is realized from amorphous precursor.

The third phenomenon consists in acceleration of the phase formation at lower temperature and for shorter time if temperature of the sample under synthesis is increased continuously. Such effect was observed in process of borates RBO_3 and garnets $R_3M_5O_{12}$ synthesis. It was established that the initiating effect of the continuous heating on synthesis of the garnets, which have cubic structure for all R-atoms only, is realized in more rapid growth of the crystallites from nano- to micro-sizes. For the borates which have a few different phases in dependence of R-atom used the continuous heating brings to formation together with equilibrium phase the new phases known for other rare earth elements.

The fourth phenomenon is the effect of "structure infection". Such effect was observed at first stages of YBO_3 crystallization after adding a few percents of Sc atoms in amorphous precursor. In this case calcite phase of YBO_3 is formed. However it is unknown for yttrium borate but is stable phase for $ScBO_3$. Almost the same situation is observed in the process of $YAlO_3$ perovskite phase synthesis. The hexagonal phase of $YAlO_3$ can to form at first steps of crystallization (T~600 C) after adding a small amount of La_2O_3 (hexagonal structure) in amorphous precursor while such phase is known in micro-dispersed state at T>1400 C only.

Keywords: nanocrystal, rare-earth compound, X-ray

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Improvement of crystal qualities by solution stirring techniques

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Solution stirring techniques are effective to make crystals with high quality, and widely introduced in industrial field. We have succeeded in growing high quality $CsLiB_6O_{10}$ and DAST by utilizing solution stirring techniques.[1] These results show that availability of the stirring techniques covers not only inorganic materials but also organic materials. In this presentation, we will introduce effects of solution stirring on GaN crystals and some protein crystals (hen-egg white lysozyme (HEWL) and glucose isomerase (GI)). Comparison of these results will show some mechanisms how the solution stirring techniques improve the crystal qualities.

We introduced sodium flux method to grow GaN single crystals.[2] Using this method, GaN can be grown by the dissolution of pressurized nitrogen gas into Ga–Na melt under conditions of approximately ~1143K and 3.4 MPa. Growth condition easily becomes unhomogeneous in a crucible, then some problems such as unfavorable nucleation, non-uniform crystallization on templates and low yield happen. We must comprehend and control solution conditions to reduce these problems. As a first step we investigated a condition in a crucible. To know the condition distribution in the crucible, we grew some of GaN crystals concentrically in the crucible. A main parameter was solution stirring, that is (1) no stirring, (2) stirring by rotation of a chamber, (3) stirring by fluctuation of a chamber. Sizes, morphologies and surface conditions of these grown crystals reflect a distribution of the supersaturation. As a result, both of the stirring techniques effectively suppress unfavorable nucleation and achieve faster growth rate than no stirring system. Furthermore solution stirring improved polycrystals and skeletal crystals. These results are obvious evidences for homogenized solution conditions.

In the field of crystallography of protein crystals, crystallographers must consider many conditions and usually use a protein solution of less than 10 μ in each batch. Thus we applied specially designed rotary shaker to introduce stirring in protein crystal growth. Crystallization plates were set on the rotary shaker, and stable solution flow arose in each batch.[3] In the case of protein crystal growth, surface kinetics can be a late-determining process in many cases, because of the difficulty of accurate molecules rotation and incorporation into crystals. Actually shapes of crystals with or without stirring were almost same in both the case of HEWL and GI. However, densities of defects were strongly affected by solution stirring. The defects densities were estimated by crystal etching. Two kinds of etch pits on HEWL and GI crystals were observed after etching. One is a shallow pit, which indicates the micro defects such as impurities or holes,[4] and the other is deep pit, which indicates the dislocations in crystals. The shallow pits' density tended to decrease with stirring speed. This tendency implies that transportation of impurities, which can be the micro defects, to crystal surface is suppressed by solution stirring. We have succeeded to improve the quality and size of some protein crystals by introducing the stirring method.[5] The decrease of shallow pit density probably is a contribution factor for crystal quality improvement.

As seen above, the way to stir solution and main effects of stirring depend on materials. In the case of GaN crystals, stirring contributed to uniformize solutions in crucible, and in the case of protein crystals, the decrease of micro defects was a main effect of stirring. However, we would like to emphasize that solution-stirring techniques finally improved crystal qualities. Solution stirring is one of a universal principle that is applicable to various materials.

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Keywords: solution stirring, GaN, protein crystal

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Mechanical property measurements of growing lysozyme crystal by atomic force microscopy with laser confocal differential interference microscopy

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We have studied combination of optical microscopy (OM) and atomic force microscopy (AFM). One of the combinations was the seamless observation of OM and AFM [1]. We observed the surface of a potassium dihydrogen phosphateIn (KDP) crystal by transmission optical microscopy, the laser confocal differential interference microscopy (LCM-DIM, [2]), and AFM. In that study, the LCM-DIM played important role as an intermediary because of its high z-axis resolution. Another study was about the interferometric microscopy using AFM cantilever. We demonstrated the observation of growing steps with measuring the step height [1]. In addition, we also demonstrated measurement of refractive index of pure water by measuring the distance between the interference fringes [3]. The point was its measurement area, which was about 10-micrometer-square region. In this study, we focused on measurements of mechanical

property by using AFM with an in-situ observation by using LCM-DIM. We chose hen-egg white (HEW) lysozyme as a model crystal because we can control the damage of the crystal surface by using AFM cantilever. One study was to determine the minimum force for making a hole on the surface by nano-indentation.

Seed crystals of lysozyme were prepared by a batch method. Six times re-crystallized egg-white lysozyme (Seikagaku Kogyo Co. Ltd.) was used without further purification. The buffer solution was 50mM sodium acetate (pH 4.5) and the precipitant was 25 mg/ml NaCl. Super-saturated lysozyme solution of 120 mg/ml was incubated at 20 ºC for 24 hours. The small seed tetragonal crystals grew in the solution. Some seed crystals with the mother liquid were placed on a cover glass in a thermal controlling cell with 60 mg/ml lysozyme solution.

The method for operating the hybrid microscope was almost the same as our previous study [1]. We used a hard AFM cantilever (NCH, NanoWorld). The spring constant of the cantilever was about 35 N/m. Sensitivity of AFM piezoelectric device was determined by the slope of force curve of a glass plate and was about 25 nm/V. Then the approaching force was calculated by their product, which was about 0.9 μN/V. We operated the AFM in a contact mode. The cantilever firstly positioned 50 μm above the surface. Then we approached the cantilever with different forces between 0.09-1.8 μN. The cantilever approached, stayed for 5 sec, and retracted. We observed the surface using LCM-DIM during the process.

We obtained the following results: Stronger force enabled us to observe a small spot (about 50 nm in diameter) where the cantilever tip was placed. This spot was disappeared after several ten seconds. The boundary force was different between increasing and decreasing the force. The observation of spot started from 1.3 μN when the force was increased and ended at 0.5 μN when it was decreased. This indicate that measured forces had two meanings. The value of 1.3 μN means the force that the tip digs the crystal. On the other hand, the value of 0.5 μN may be the crash force of the lysozyme attached on the tip.

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Keywords: AFM, optical_microscopy, surface_process

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The nanoscale composite nature of biological carbonate skeletons

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In order to highlight the composite nature (Figs. 1a, 1b), the nanoscale internal structure (Figs. 1c, 1d) and the interface between the bioinorganic and polymer components in carbonate biological materials we performed dissolution experiments in an AFM cell and monitored the changes with AFM (Figs. 2a, 2b). The investigated samples were shells of modern calcitic brachiopods and the teeth and spines of modern sea urchins. By using different solutions in the AFM cell, both components, the organic as well as the inorganic component within the skeleton could be dissolved selectively (Fig. 2b). The mineral phase was dissolved by using destilled water, the organic polymers within the skeletons were digested and removed from the skeleton with the enzymes trypsin and chitinase. The resulting morphology highlighted the dissolved and the remaining undissolved components (Fig. 2b). Thus the nanoscale structure of both, the inorganic and the organic components as well as their dissolution behavior and distribution pattern in the skeleton could be highlighted and monitored in-situ.

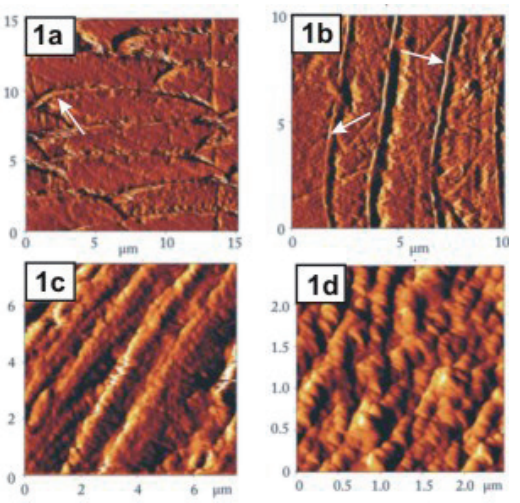

Figure 1. Arrays of transversally (1a) and longitudinally (1b) sectioned brachiopod fibres in the shell of the modern brachiopod *Magellania venosa* (1a, 1b). The fibres are lined by organic sheaths (white arrows in 1a and 1b) and have an internal granular nanostructure (1d).

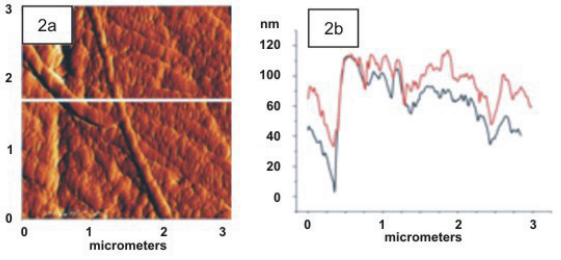

Figure 2. Dissolution of brachiopod calcite for 1 hour by destilled water. Fig. 2b shows the height of the sample at the position of the white line in Fig. 2ba before (red graph in 2b) and after (black graph in 2b) the dissolution experiment. The difference in height shows that water has dissolved the calcite phase in contrast to the organic sheaths around the fibres.

Keywords: nanostructure, organic inorganic interface, AFM.

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Step interlacing on the (100) face of retgersite crystal

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Step interlacing phenomenon is natural for a number of organic and inorganic crystals. It is known step interlacing interpretations of F. Frank [1] and W.van Enckevort [2]. But question of dislocation spiral formation was left out so far.

The central part of growth hillock on the (001) face of retgersite crystal (NiSO4.6H2O) was visualized by in-situ AFM method.

The model of dislocation spiral formation with step interlacing is proposed in this work. It is based on rectangular critical nucleus turn in accordance with screw symmetry axis of fourth order. Thickness of each of 4 layers is equal to ¼ parameter c. The center of turning serves as asymmetrical equilibrium point of Wulf's theorem. Different speed anisotropy of layers causes the separation of fast lower layer from slow upper one and the brakeage of fast upper layer on slow lower one. In chime with experiment on hillock slope in echelon steps have height of unit c and at angles of polygonized hillock interlacing steps have heights of ¼ and ¾ unit c, correspondingly.