

## Magnetic alignment: method and its applications to structure analyses

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Diamagnetic and paramagnetic (commonly called non-magnetic) materials do respond to external magnetic fields though their response is very small compared to that of ferromagnetic materials. If these materials have magnetic anisotropy, like crystals, we can make them align by magnetic fields. Under static magnetic fields, their easy axis aligns parallel to the applied field, while under rotating magnetic fields, their hard axis aligns parallel to the axis of the field rotation. By combining static and rotating magnetic fields, the easy and hard axes are aligned simultaneously (biaxial alignment). This alignment can occur to biaxial crystals (triclinic, monoclinic, and orthorhombic).

The magnetic alignment competes with thermal fluctuations. It is necessary to overcome the thermal fluctuations that the anisotropic magnetic energy should largely exceed the thermal energy. This condition is typically satisfied for microcrystals of ca.  $\mu\text{m}$  sizes exposed to ca. 10-T magnetic field although these parameters strongly depends on the magnetic anisotropy of microcrystals under consideration and what level of alignment we want to achieve. There are various types of combinations of static and rotating magnetic fields (modulated magnetic fields<sup>1-6</sup>) to produce biaxial alignment of superconducting materials,<sup>2,5</sup> ceramics,<sup>4</sup> inorganic crystals,<sup>7</sup> organic,<sup>8</sup> and protein<sup>9,10</sup> crystals. Aligned specimens are prepared by mixing microcrystalline powders in liquid matrix to obtain a suspension and subjecting the suspension to modulated magnetic fields, followed by consolidation of the matrix to obtain polymer composites in which microcrystals are 3-dimensionally oriented. We call this composite magnetically oriented microcrystal array (MOMA) (Fig. 1). Actually, it is difficult to produce modulated magnetic fields; instead, a suspension is rotated in a modulated manner in a static magnetic field.

Biaxial alignments of microcrystals are useful in various areas of science and technology. Among them, we have applied the magnetic alignment to X-ray diffraction and solid state NMR measurements.<sup>11</sup> Due to the 3-dimensional microcrystal alignment, MOMAs can exhibit X-ray diffraction that is equivalent to that obtained from a real single crystal of the same compound. This means that we can perform single crystal X-ray structure analyses from microcrystalline powders (Fig. 1). Powders are conventionally analyzed by the powder method that is complicated and indirect compared to the single crystal method. The MOMA method is of great help when one wants to perform single crystal analyses but lacks in large single crystals. MOMAs might be much more useful for neutron diffraction measurements because mm-size single crystals are required there.

Solid-state NMR is a powerful means to understand the electron distribution around specific atoms under consideration. This information is obtained through chemical shift tensors for these atoms. In conventional CP (cross polarization) / MAS (magic angle spinning) solid-state NMR, where microcrystalline powders are used, only the average of three principal values is obtained. There are several advanced pulse techniques used to determine the individual principal values, but the determination of principal axes is yet difficult. If large single crystals are available, the principal axes are determined by using single-crystal solid-state NMR technique. We have demonstrated that MOMAs can work instead of large single crystals and determined the principal axes of <sup>13</sup>C and <sup>31</sup>P from microcrystalline powders.<sup>12, 13</sup>

We have also developed MOMS (magnetically oriented microcrystal suspension) method, by which single crystal X-ray measurements can be performed in-situ, without solidifying the matrix suspending liquid.

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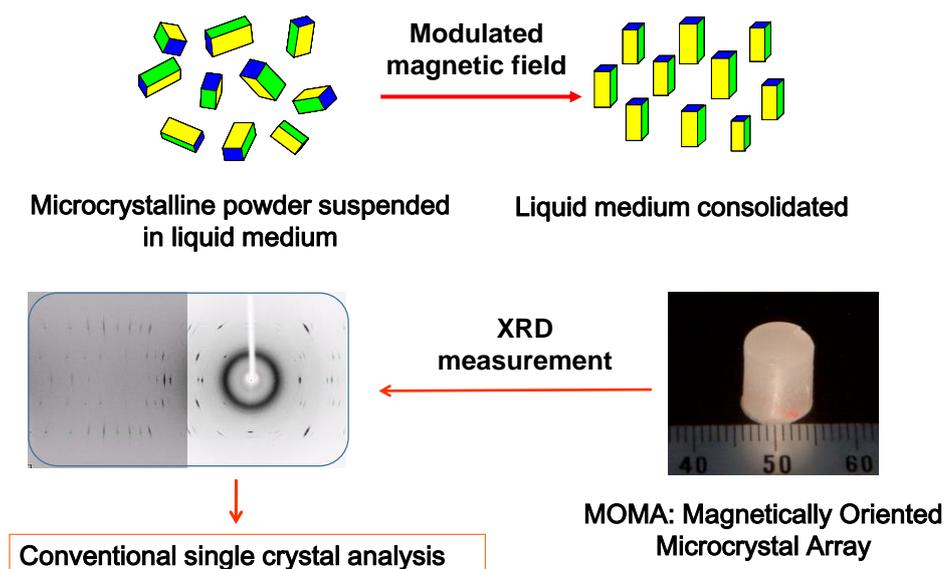


Fig. 1 Schematic of preparation of MOMA (magnetically oriented microcrystal array) and its X-ray diffraction from which the crystal structure is determined by using conventional single crystal analyses.

# Liquid Crystal Electrochemical Polymerization under Magnetic Field

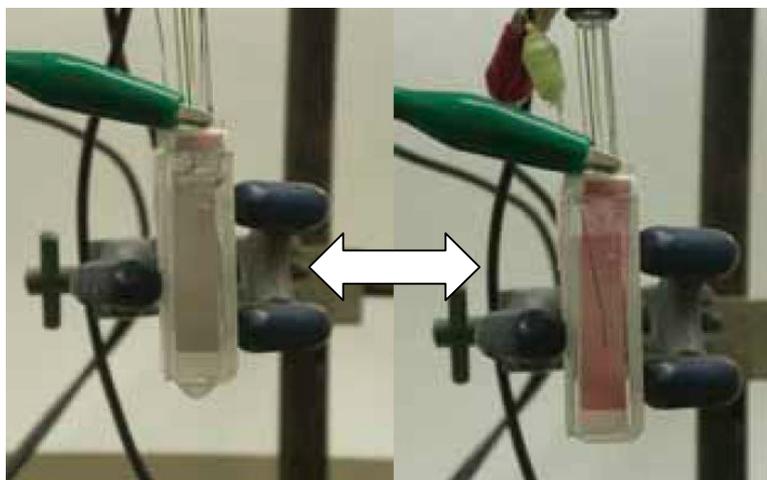
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## Liquid crystal electro-polymerization

Optically active conjugated polymers were prepared by electrochemical polymerization of achiral monomers in a cholesteric liquid crystal (CLC) electrolyte solution [1,2]. The polymer films thus synthesized exhibited circular dichroism (CD). This method can be referred to as "chiral electrochemical polymerization".

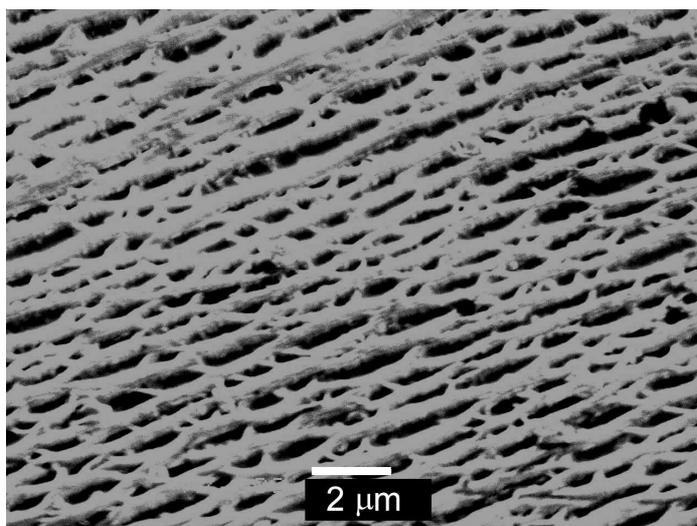
In the present report, the chiral electrochemical polymerization of thiophene derivatives by using CLC electrolyte containing cholesteric derivatives as chiral inducer was carried out. The surface morphology of the polymers was confirmed with polarizing optical microscopy observations. The polymers show not only electrochromism (Figure 1) but also "chiral electrochromism". Change in the optical rotation of the polymer depends on the redox conditions. The ellipticity of this polymer is also found to exhibit hysteresis with redox cycle. The results indicate that the optical rotation of chiral polymer can be tuned through electric field by electrochemical method.



**Figure 1.** Electrochemical doping (oxidization) and dedoping (reduction) of the chiral polymer film in 0.1 M TBAP/acetonitrile solution. Left: +1.2 V, right: 0 V.

## Electro-polymerization in liquid crystal under magnetic field

Liquid crystal can be oriented along the magnetic field. Oriented liquid crystal prepared by magnetic field provides oriented chemical reaction field. In this case, the liquid crystal electrolyte solution plays a role of uniaxial polymerization environment. Resultant polymers synthesized in the oriented liquid crystal show uniaxial oriented form confirmed with scanning electron microscopy (Figure 2). Polarized absorption spectra of the polymers thus prepared demonstrated anisotropy. Furthermore, "linear polarized electrochromism phenomenon" was found [2]. The polymer shows electrochromism by application of voltage, which change the color with linear dichroism.



**Figure 2.** Scanning electron microscopy (SEM) image of the polymer prepared with liquid crystal electrochemical polymerization under magnetic field.

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## Control of crystallographic orientation in bulk ceramics by colloidal processing in a high magnetic field

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Tailoring the crystallographic orientation in ceramics is very useful for improving their properties. Many researchers have reported that the textured ceramics were produced by the Templated Grain Growth method (TGG), hot forging, one directional extrusion, etc. In this presentation, a magnetic field is shown to be very effective in controlling the crystallographic orientation in bulk ceramics. We reported that the colloidal processing in a strong magnetic field was able to control the crystallographic orientation even in diamagnetic ceramics. In this process, a strong magnetic field is applied to the particles in a stable suspension. The particles were rotated to an angle minimizing the system energy by a magnetic torque generated from the interaction between the magnetic anisotropy and the applied magnetic field. In this processing, dispersion of powders in a suspension is necessary to effective work of a magnetic field, because large interaction between the agglomerated particles restrains the powder in a suspension from rotating by a magnetic field. Colloidal processing was used for particle dispersion in this study because of developing for consolidating fine particles to avoid heterogeneous agglomerates by electrostatic repulsion due to surface charge.

In the case of  $\text{Al}_2\text{O}_3$ ,  $\text{SiC}$  and  $\text{LiCoO}_2$ , the  $c$ -axis of hexagonal crystal structure aligned parallel to the magnetic field. The thermal conductivity parallel to the  $c$ -axis was higher than that perpendicular to the  $c$ -axis in textured  $\text{SiC}$ . In the case of  $\text{AlN}$ ,  $\text{ZnO}$  and  $\text{Si}_3\text{N}_4$ , we confirmed that the  $a$ -axis aligned parallel to the magnetic field. The rotating magnetic field was used to control the development of the  $c$ -axis orientation in order to improve the thermal conductivity.

If the orientation axes of platelet particles aligned due to a geometrical effect and a magnetic field are different, the multi-dimensional orientation can be controlled by simultaneous use of both the effects, and control of the elaborate microstructure will be expected. Figure 1 shows that the pole figure in  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  prepared by slip casting in a magnetic field with platelet particles. The  $\{001\}$  pole figure on T plane perpendicular to the casting direction and parallel to the magnetic field shows a very strong spot at the center, which indicates that the  $c$ -axis was aligned parallel to the casting direction. The  $\{100\}$  pole figure exhibits a couple of strong spots at the points of  $90^\circ$  from the center along the latitude line. The  $\langle 100 \rangle$  texture was aligned parallel to the magnetic field. Since the  $c$ -axis and the  $\langle 100 \rangle$  axis orientation can be simultaneously controlled.

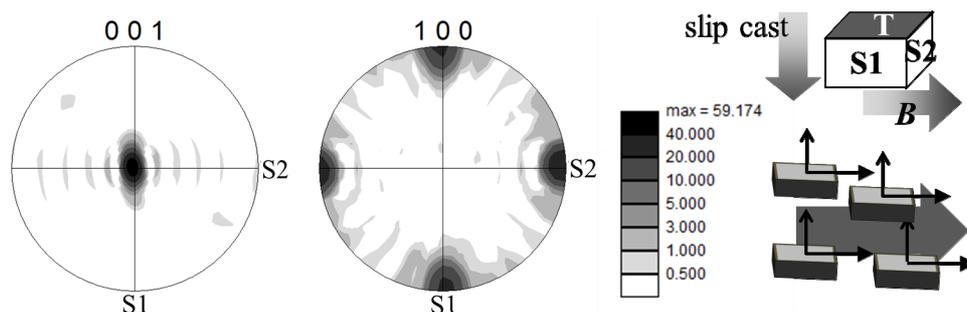


Fig. 1 Pole figure on T plane perpendicular to the slip casting direction in  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  prepared by slip casting in a magnetic field with platelet particles.

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## Micro-domain control toward new lasers

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The solid-state lasers and nonlinear optics have contributed to broadening the new horizon in quantum electronics, owing to their high-brightness nature of giant pulses under Q-switching and mode locking<sup>1)</sup>. Moreover, their cutting edges are expected from the field of high-energy physics (i.e., laser fusion/laser ignition, laser accelerator, and vacuum decay) to precise measurement, laser-based material processing, and laser ignitions (i.e., engine ignition and fusion ignition). On the other hand, its development has long been a materials-limited. In this talk, we'd like to review the recent progress of **Micro Solid-State Photonics** with regard to high performance microchip lasers based on the micro-domain structure and boundary-controlled materials<sup>2,3)</sup>. The past decade has witnessed a veritable revolution in the types and performance levels of solid-state lasers, largely due to development of micro-domain engineered new optical materials, such as the transparent laser ceramics. Especially, the naturally bonded composite Nd:YAG/Cr:YAG ceramics contributes sub-ns giant pulse generation. These progress of YAG ceramics enabled multi-megawatt microchip lasers, sub-PW/sr-cm<sup>2</sup> brightness and sub-ZK brightness temperature. “The world first laser ignited car” has been demonstrated by it<sup>4)</sup> (Fig. 1). And furthermore, we'd like to discuss the next generation of high-brightness lasers based on the aligned anisotropic ceramics by RE<sup>3+</sup>-ion, such as Yb:FAP ceramics. The fabrication of laser-grade anisotropic ceramics by a conventional sintering process is not possible owing to optical scattering at randomly oriented grain boundaries. We have demonstrated the first realization of transparent anisotropic ceramics by using a new crystal orientation process based on large magnetic anisotropy induced by 4f electrons (Fig. 2). By slip casting in a 1.4 T magnetic field and subsequent heat treatments, we could successfully fabricate laser-grade calcium fluorapatite ceramics, and its laser oscillation to complete the laser ceramics map as shown in Fig. 3<sup>3,5,6)</sup>. These compact lasers can provide the extreme giant-power by using micro solid-state photonics, so to speak “**Giant Micro-photonics**”<sup>1,2)</sup>.

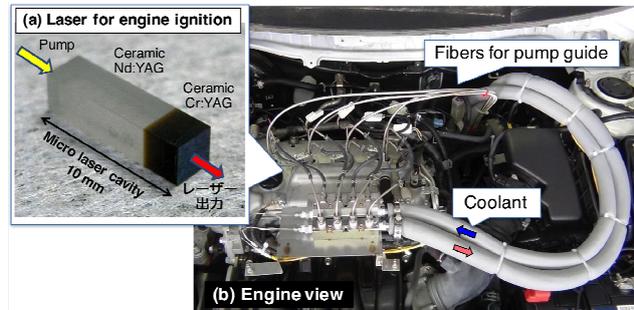


Fig. 1. The world first laser ignition engine car by the giant pulse micro laser in Nd:YAG/Cr:YAG transparent laser ceramics.

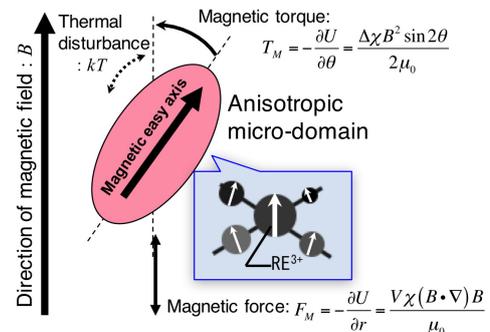


Fig. 2. Schematic of the RE-assisted magnetic orientation method for fabrication of RE-doped anisotropic laser ceramics

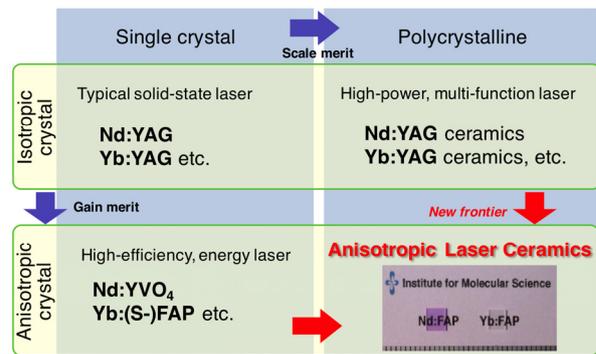


Fig. 3. Progress map of solid-state lasers from isotropic single crystals to anisotropic laser ceramics.

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## Crystal alignment by imposing a magnetic field during solidification

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Alignment of crystals having an anisotropic unit cell structure can enhance anisotropy of physical, chemical and/or biological properties, and thus a lot of investigations on the crystal alignment have been done for many industrial applications. One of the crystal alignment methods is imposition of a magnetic field on the crystals under the condition that they can rotate to reduce magnetization energy. In this presentation, improvement of thermoelectric property of higher manganese silicide having a chemical formula of  $\text{MnSi}_{1.73}$  synthesized by solidification under the imposition of the static magnetic field<sup>1)</sup> and a suitable condition for crystal alignment during solidification<sup>2, 3)</sup> are mentioned. .

Pure manganese and silicon were prepared as raw materials, and they were mixed with a molar ratio of 1:1.8. The mixture was heated under argon atmosphere using an induction heating system for its complete melting to over 1773K which is higher than melting points of silicon of 1700K and manganese of 1517K, for its complete melting and it was subsequently homogenized by holding the sample at 1523K which was higher than its liquidus temperature of 1435K. Then it was cooled for synthesis of  $\text{MnSi}_{1.73}$  by the solidification under the controlled cooling rate of 2.5K/minute until 423K. The magnetic field parallel to gravitational direction was imposed on the sample from 1523K till 1273K in which the sample completely changed from liquid to solid because its liquidus and eutectic temperatures are 1435K and 1415K, respectively. After the sample reached room temperature, it was cut for evaluation of precipitated phase, degree of crystal alignment and thermoelectric properties. The primary composed phase in the samples with and without the magnetic field was  $\text{MnSi}_{1.73}$  phase. The averaged angle between the (001) crystallographic plane of  $\text{MnSi}_{1.73}$  crystals and the plane perpendicular to the magnetic field direction was 85.9 degrees in the case with the magnetic field while that was 48.1 degrees in the case without the magnetic field. This indicated that most of its c-axis was aligned perpendicular to the magnetic field direction in the sample solidified with the magnetic field. Therefore, the magnetic field imposition during the solidification introduced the crystal aligned structure. The electrical conductivity in the direction parallel to the magnetic field solidified with the magnetic field was three times larger than that solidified without the magnetic field while the Seebeck coefficient solidified with the magnetic field was 10% lower than that solidified without the magnetic field. As the result, the power factor solidified with the magnetic field was about two times larger than that solidified without the magnetic field.

For crystal alignment by imposing a magnetic field during solidification, an environment in which crystals can rotate to reduce magnetization energy is required. Solidification starts from a wall when the wall temperature is lower than the bulk temperature. This is popular in casting processes. However, dendrites grown from a wall can not rotate. Thus solids floating in a liquid is essential for crystal aligned structure formation by imposing the magnetic field. For this purpose, not only a magnetic field but also an electrical current were introduced and model experiments have been done using low temperature melting point alloys<sup>2, 3)</sup>. The simultaneous imposition of the static magnetic field and the electrical current in the initial stage of the solidification can break dendrites into pieces and the sequential static magnetic field imposition make them to reduce the magnetization energy.

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## Effect on unsteady flow on a particle orientation process in rotating container under high magnetic field

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Because of recent development of superconducting magnet, attention has been given to magnetic alignment. This technique aims at improvement of physical properties by controlling the direction of particles and crystals. When a particle with magnetic anisotropy is applied a rotating magnetic field, the smallest axis of magnetic susceptibility is aligned to the axis of rotation. In current studies, a container with particles which are dispersed in solvent is rotated in a static magnetic field in order to apply a rotating magnetic field. When a container with liquid is started to rotate or stopped, unsteady flow occurs in the suspension. Therefore, we have simulated unsteady flow of the suspension in a rotating container by CFD and examined the effect of the unsteady flow on the magnetic orientation process through numerical simulation<sup>1)</sup>.

This study considered the flow of fluid in a cylindrical container filled with liquid without particles and assumed axisymmetric flow. The size of the container is  $r_0 = h = 20$  mm, the angular velocity of the container is  $\Omega = 2\pi$  rad/s and the solvent is water. Figure 1 shows the streamline in a rotating container at  $t = 1$  s from the start of rotation. This result indicates that the flow occurs in vertical section of a rotating container. Next, we investigated the effect of the flow on an oriented rod-like particle under rotating magnetic field  $\mathbf{B}$ . We assumed polyethylene fiber<sup>2)</sup> with a diameter  $d$  and a length  $l$  and anisotropic susceptibility  $\Delta\chi < 0$ , as shown in Figure 2. In case of continuous rotating magnetic field, a rod-like particle is finally aligned parallel to the axis of rotation because the unsteady flow disappears as time goes by. However, in case of modulated rotation magnetic field<sup>3), 4)</sup>, the unsteady flow occurs each time the angular velocity is modulated. As a result of this, an oriented rod-like particle will always be affected by the unsteady flow.

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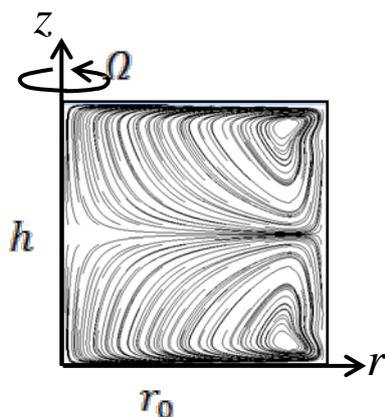


Fig. 1 The streamline in a rotating container at  $t = 1$  s.

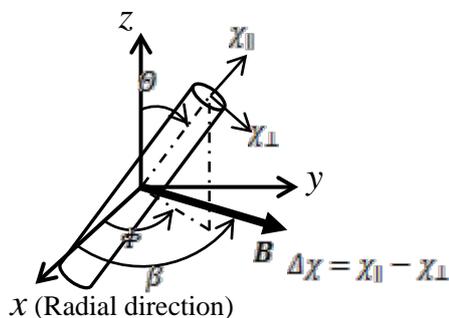


Fig.2 An axisymmetrical particle.

# Measurement and control of biological microcrystals by magnetic field and light

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In animal kingdom, there should be huge number of unrevealed functions of biological materials. Biochemical functions of these materials attracted many researchers and the results of research have already been provided to an industry. In contrast, physical properties, such as magnetic and optical property, of the biological materials are less clarified. One of the mechanism of magnetic field effects is magnetic orientation. The magnetic orientation can be observed in diamagnetic materials as well as strong magnetic materials. The required conditions for rotating the diamagnetic materials are distinct diamagnetic anisotropy and diamagnetic torque energy exceeding the thermal agitation in room temperature. Microcrystals are one of the candidates of dia-magnetically controllable target by utilizing a conventional magnetic fields (less than 500 mT).

At present, some kinds of biogenic microcrystals were found to be magnetic field responsible even though they did not contain effective amount of para- or strong- magnetic materials. A biogenic crystal containing guanine, which is produced in iridophore of fish skin, is biochemically designed to act as a *bio-reflector*, and it was revealed that the guanine crystals in many species of fish are distinctly responsible to the magnetic fields of more than 100 mT ~ 200 mT. The newly discovered light reflecting anisotropy in the guanine crystals enabled the detection of magnetic rotation [1]. Recently, as a kind of biomimetic approach, we are investigating guanine crystals in deep sea fishes, as shown in Fig. 1, those should have an effective light control mechanism which might be useful for our industry.

The guanine has relatively high reflective index (~1.8) and can obtain distinct diamagnetic anisotropy when they form a platelet. We can expect same kind of light reflecting control by magnetic fields in other type of biogenic crystal. For example, coccolith disk, a calcium carbonate crystal generated in the phytoplankton *E. huxleyi* oriented under the magnetic fields [2].

The introducing magnetic study on biogenic microcrystals can provide a new control method for tunable color control.



Fig. 1. Silver shining in a deep sea fish.

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