Magnetic Orientation of Diamagnetic Particles

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Diamagnetism originates from the motion of electrons induced by a magnetic field and all materials have this magnetic property. Diamagnetism is much weaker than ferromagnetism and is usually difficult to detect and utilize. The diamagnetic energy of a particle in a magnetic field is proportional to the volume V and diamagnetic susceptibility χ of the particle, and the square B^2 of the applied magnetic field. This energy is comparable to the thermal energy kT at room temperature if the particle is about 1 μm in size and B is about 10 T. Under these circumstances, the orientation of the particle can be maintained by the magnetic field against the randomizing force of thermal agitation. Although the diamagnetic orientation of particles has been known for a long time, it did not attract scientists and engineers until high magnetic field such as 10 T became common. At 10 T, the magnetic energy is 100 times larger than at 1 T, increasing the chance of finding orientation of a variety of materials[1,2].

Diamagnetism is described by the magnetic susceptibility tensor, a second rank tensor similar to the dielectric and optical tensors. Symmetry in diamagnetism is equal to or higher than crystal symmetry (Neumann's Principle). This is in contrast to ferromagnetism. The diamagnetic symmetry of crystals is characterized by (a) isotropic, (b) uniaxial, and (c) biaxial ones. Cubic crystals belong to (a), trigonal, tetragonal, and hexagonal crystals to (b), and orthorhombic, monoclinic, and triclinic crystals to (c). These features are common to physical tensors of the second rank. The magnetic field only allows biaxial orientation at most.

Diamagnetic anisotropy of a particle is described by the magnetic susceptibility tensor, χ_1, χ_2, and χ_3 ($\chi_3 < \chi_2 < \chi_1 < 0$), and the corresponding magnetic axes. The χ_1 is called the easy axis following the notation for ferromagnetic materials. In a biaxial crystal, the three magnetic χ_1-, χ_2-, and χ_3-axes correspond to the three crystallographic a-, b-, and c-axes. In a static magnetic field, χ_1-axis aligns parallel to the magnetic field, and in a rotating magnetic field, χ_3-axis aligns parallel to the field rotating axis. Furthermore, three-dimensional crystal alignment is possible if a time-dependent magnetic field is applied (Fig. 1)[3,4]

Magnetic orientation is a useful tool in materials science[1,2]. Micro- to nano-scale fibers, crystals, and particles can be easily oriented in matrices to form composite materials with high anisotropy. Flexible heat diffusion plastic sheets, in which carbon fibers are oriented perpendicular to the sheet surface, are commercialized.

Magnetic orientation is also useful for various spectroscopic studies. Biaxial microcrystals can be aligned three-dimensionally to create pseudo single crystal which we call “Magnetically Oriented Microcrystal Array” (MOMA). In MOMA, three-dimensionally oriented microcrystals are embedded in a solid matrix. Since the X-ray diffraction from MOMA is equivalent to that from actual single crystal, the single crystal analysis is possible from powder samples. We have determined the crystal structures of inorganic and organic compounds, and proteins from powder samples using the MOMA technique[5]. MOMA is also used for single-crystal solid-state NMR[6] and ESR.

For MOMA, it is difficult to recover the sample crystals after measurement because the microcrystals are embedded in the matrix resin. This is a disadvantage of this method. To avoid this, a method called "Magnetically Oriented Microcrystal Suspension" (MOMS) was developed[5]. In this method, X-ray and NMR measurements of a suspension of magnetically oriented microcrystals are performed in-situ, which facilitates sample recovery.

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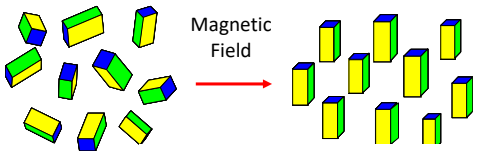

Fig. 1 Three-dimensional magnetic orientation of microcrystals

Field-induced rotational oscillation of diamagnetic and paramagnetic materials caused by a permanet magnet

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A number of magnetic effects have been reported on weak magnetic materials, which required strong field intensities above the level of several Tesla. To realize such application at a low field intensity, it is important to adopt reliable values of χ and $\Delta\chi$ assigned to individual materials in designning the experiment of magnetic effects.[1] In order to obtain $\Delta\chi$ from a small sample, rotational oscillation of magnetically stable axis with respect to static field B was observed;[2] here sample was released in an maicrogravity are. From the period of oscillation τ , $\Delta\chi$ of a small particle is detected, and intrinsic $\Delta\chi$ assigned to individual material was obtanable without measuring mass $m$of sample. Value of τ is deduced from a field anisotropy energy $\frac{1}{2}\Delta\chi m B^2$ as

$$\tau=2\pi(I/m\Delta\chi)^{1/2}B^{-1}; \qquad (1)$$

moment of inertia of the crystal is defined as I. A compact magnetic circuit consisting of small Nd magnetic plates was effective to produce the magnetic field area in a limited area. It is seen in eq.(1) that τ is independent to m, and it is possible to deduce $\Delta\chi$ form τ, I/m and $|B|$ no matter how small the crystal may be. Using this system, $\Delta\chi$ above 5×10^{-10} emu/g is measurable from a submillimeter size sample, and $\Delta\chi$ is obtained for most existing materials.[3]

Using this system, $\Delta\chi$ was detected for the first time in amorphous silica, which has been considered to posses negligibly small anisotropy. This $\Delta\chi$ appears in a limited region of the silica surface formed by rapid cooling of a melt precursor, and is expected to provide a quantitative data in elucidating the origin of interstellar dust alignment. By improving spatial resolution of the system, extent of structural deformation with respect to bulk material can be estimated for particles in the nano-region, because $\Delta\chi$ directly correlates with the configuration of chemical bonds.[2,4]

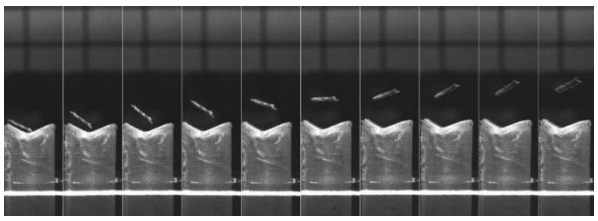

Fig.1 Sequential image of field induced oscillation observed in a sheet silicate crystal.[1,2] Time interval between the images is 0.033 s. Homoneneous field of B = 0.056T is applied in a horizontal direction of the image. The crysal has a planer shape with its plane parallel to c-plane, Rotational-oscillation of c-plane with respect to direction of field is seen in the figure..

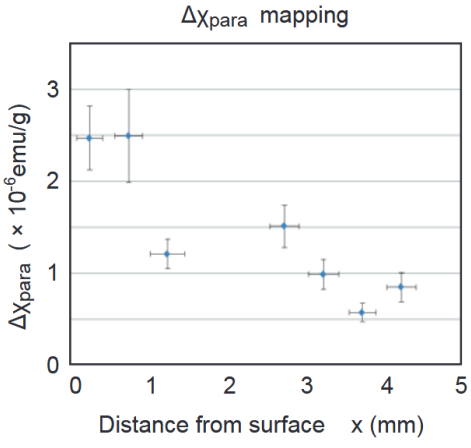

Fig.2 Depth profile of $\Delta\chi$ observed at the surface of synthetic silica[3].

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Recent progress in three dimensional magnetic alignment techniques

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In materials science, technologies of crystal growth are indispensable from the viewpoint of the improvement of functionalities of their functional materials. A typical method of the single crystal growth is based on the epitaxial growth technique such as melt-solidification using seed crystal and thin film growth on single-crystalline templates. Our group focuses on biaxial grain-orientation using by a modulated rotating magnetic field (MRF)[1]. In principle, this technique is extensively applied for various polycrystalline functional materials with tri-axial magnetic anisotropies. Moreover, the magnetic alignment method using MRF is a room-temperature process, and it does not require seed crystals and single-crystalline templates. Appropriate substances for the magnetic alignment are expected to be further expanded by the use of 10-tesla-class magnets. However, in order to raise the magnetic alignment process using MRF to the practical stage of a material-production process, it should be improved as a continuous production process. Recently, our group developed an equipment that can generate a linear drive type of MRF [2] for tri-axial magnetic alignment applicable to a continuous production process. This equipment can generate a kind of MRF by reciprocating an arrayed magnet unit assembled using permanent magnets.

Figure 1(a) shows a fundamental concept for designing the arrayed magnets in the linear drive type MRF generation system. It is important to create a magnet array with two different portions of bending magnetic field from downward to upward directions and uniform magnetic field which points upward or downward in a space between top and bottom array by designing the top and bottom parts of the array using permanent magnets. In details, it is expected, by the reciprocating motion of the magnet array, that static magnetic field is generated for the regions ①－③ and ⑤－⑦, and rotating magnetic field is generated for the region ③－⑤. Therefore, it leads to the generation of MRF. Figure 1(b) shows an example of the arrayed Nd-Fe-B magnets, which is obtained from simulation by FEM. In practice, the two different regions of magnetic flux can be seen in the space between upper and bottom arrays. At the current stage, MRF with a static magnetic field component of 0.9 T and a rotating magnetic field component of 0.5–0.9 T and 350 rpm has been successfully generated. Moreover, biaxial alignments of orthorhombic $DyBa_2Cu_3O_y$ (y~7) superconductor powders cured in epoxy resin and dried from a slurry have been achieved. It is indicated that the magneto-scientific process is a candidate of practical production methods of superconducting bulks and tapes.

In this presentation, in addition to the above topics, simulation research on the design of the magnet arrays using a concept of magnetic circuit will be reported. This work was partly supported by Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP), Japan Science and Technology Agency (JST) and JSPS KAKENHI Grant Number JP17H03235.

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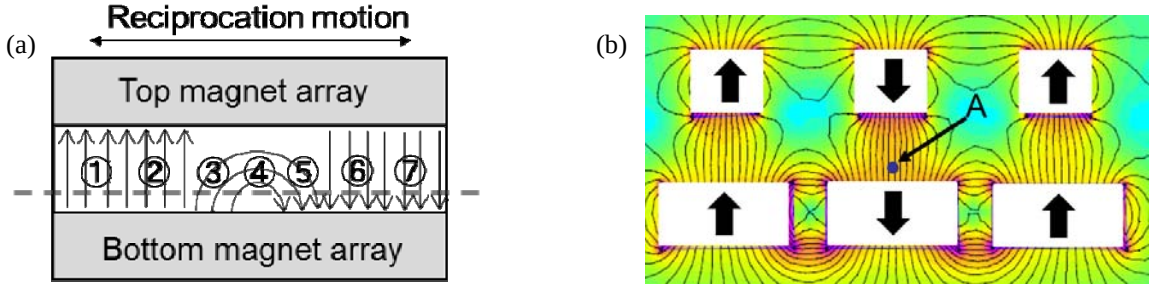

Figure 1. (a) A conceptual magnet array for the linear drive type MRF generation system. (b)Distribution of magnetic flux in a magnet array. This simulation result was obtained by the FEMM software.

Control of the orientation of inorganic particles in a magnetic field by addition of metal elements

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In the orientation method using a high magnetic field, particles are oriented using a slight magnetic anisotropy to prepare a particle-oriented powder compact. The crystal-oriented ceramics was obtained by sintering the particle-oriented powder compact, and it was expected that the property would be improved by the crystal orientation. In the case of a diamagnetic material, the crystal direction with a large diamagnetic susceptibility is perpendicular to the magnetic field. A rotating magnetic field is used to direct that crystal axis in one direction. We reported the c-axis orientation of tungsten bronze oxide crystals and hydroxyapatite by applying a rotating magnetic field[1]. However, since the rotating magnetic field is a batch process and is not very suitable for continuous production, it would be a great advantage if the orientation direction of the substance could be changed. Horii et al. have reported that the anisotropy of magnetic susceptibility is changed by adding various rare earth ions to superconducting materials [2]. In the presentation, we will introduce the effect of adding metallic elements on the magnetic field orientation of hydroxyapatite and mordenite zeolite crystals. Hydroxyapatite (Hap) considered Europium (Eu) as an additive. For mordenite zeolite particles, we investigated the effects of transition metals in addition to rare earth metals. See reference (3) for more detail information on mordenite zeolite particles with ion-exchanged.

Hydroxyapatite particles doped with europium were synthesized by solid reaction. After grinding and mixing raw powders in a ball milling, the dried powder was heated at 1050 °C for 4 hours. The reacted powders were ground by a ball milling in 2 propanol as a solvent and dried. A slurry was prepared using distilled water as a solvent and ammonium polyacrylic acid as a dispersant. The pH of the distilled water was adjusted to 10. This slurry was poured into a mold with a diameter of 25 mm, and a vertical magnetic field was applied to the slurry in a superconducting magnet (TOSHIBA TM-10VH10) to dry the slurry. The magnetic flux densities were 3T and 10T. The slurry of HAp alone was naturally dried in a rotating magnetic field. The powder compacts were sintered at 1150 ° C for 2 hours. The orientation of the samples was evaluated by powder X-ray diffraction, and the degree of orientation was calculated by the Lotgering method. The microstructure was observed with a scanning electron microscope.

The crystal structure of HAp that Eu^{3+} is replaced with Ca^{2+} sites has been reported, and that Ca sites are particularly frequently replaced [4], and this tendency was confirmed from Rietveld analysis. Figure 1 shows the XRD figures of HAp:Eu^{3+} prepared in a 3T magnetic field, a single HAp powder compact, and a powder compact fabricated without using a magnetic field. Due to the solid solution of Eu, the c-axis was oriented in the direction of the magnetic field in a vertical magnetic field. On the other hand, the simple HAp was oriented on the c-axis by the rotational magnetic field orientation similar to previous study. It was found that the easily magnetized axis changed due to the solid solution of Eu^{2+}, and that the magnetic field required for orientation decreased to a magnetic flux density of 3T. It is suggested that anisotropic solution of Eu contribute to oriented direction and response to the magnetic field.

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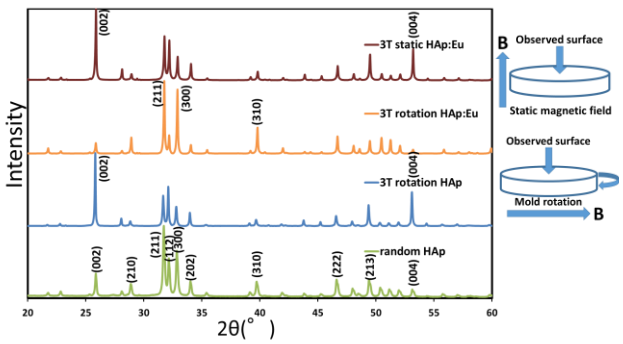

Fig.1 XRD of oriented HAp:Eu and HAp powder compact

Preparation of Crystalline Oriented Poly(L-lactide) Films by Casting in a Magnetic Field Using Ionic Liquids, and those of the Useful

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Poly(L-lactic acid) (PLLA) is harmless to the human body and exhibits unique properties such as piezoelectric effect by appropriately controlling the crystal structure of PLLA. We have found that field-induced blend films composed of PLLA and amorphous poly(lactic acid) can be fabricated by an isothermal process under a 10 T magnetic field without forming β-crystals[1)] and increasing the degree of crystallinity while maintaining the orientation[2)]. The key to this method lies in the melt viscosity of PLLA. Although PLLA films showing high orientation can be obtained by appropriately adjusting the viscosity, there were significant barriers to crystal growth while maintaining orientation.

On the other hand, we are developing novel ionic liquids (ILs) to improve the dispersion of inorganic nanoparticles in polymer matrices. PLLA was dissolved in chloroform and 1-butyl-3- methylimidazolium dibutylphosphate (IL) was added and the films were cast deposited under a 10 T magnetic field. Isothermal crystallization treatment at 90°C for 2 hours was then performed to improve the crystallinity of the PLLA film while maintaining some orientation of the PLLA film. POM observation of the oriented PLLA film (Fig. 1) showed no spherulite[3)].

In our recent work with ILs, dispersion and release have been successfully achieved[4)]. After dispersion of a complex of tetrabutylphosphonium cation and iron(III) chloride anion in a polymer matrix, iron(III) chloride could be deposited in the matrix by light irradiation. The phase transition induces magnetic properties only in the light-irradiated areas. In particular, when combined with a molecularly oriented matrix, the magnetic domains of iron(III) chloride were aligned and the magnetic susceptibility was three times higher than that of disordered iron(III) chloride. We believe that the combination of ILs with external stimuli to polymer matrices, such as crystal growth, dispersion, and phase separation while maintaining orientation, will lead to a great leap forward in the functionalization of polymeric materials.

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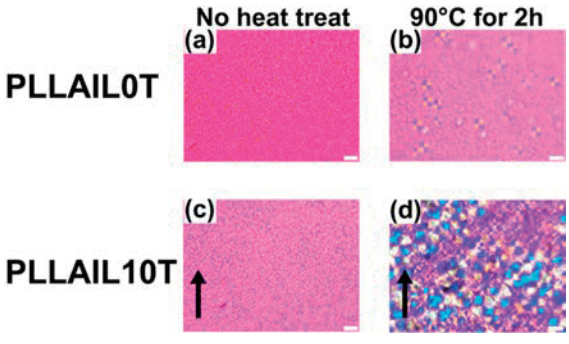

Fig.1 Polarization microscope image of PLLA films. (a): PLLAIL0T, (b): PLLAIL0T2, (c): PLLAIL10T and (d): PLLAIL10T2. Black arrow is the direction of the magnetic field.

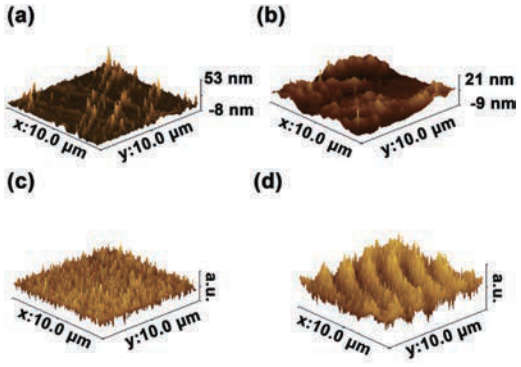

Fig 2. AFM images of each state of films: (a) After UV irradiation, (b) After UV irradiation and oriented polymer chains. MFM images: (c) After UV irradiation, (d) After UV irradiation and oriented polymer chains.