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. μm 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[1-6]) to produce biaxial alignment of superconducting materials,[2,5] ceramics,[4] inorganic crystals,[7] organic,[8] and protein[9,10] 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.[11] 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 ^{13}C and ^{31}P from microcrystalline powders.[12, 13]

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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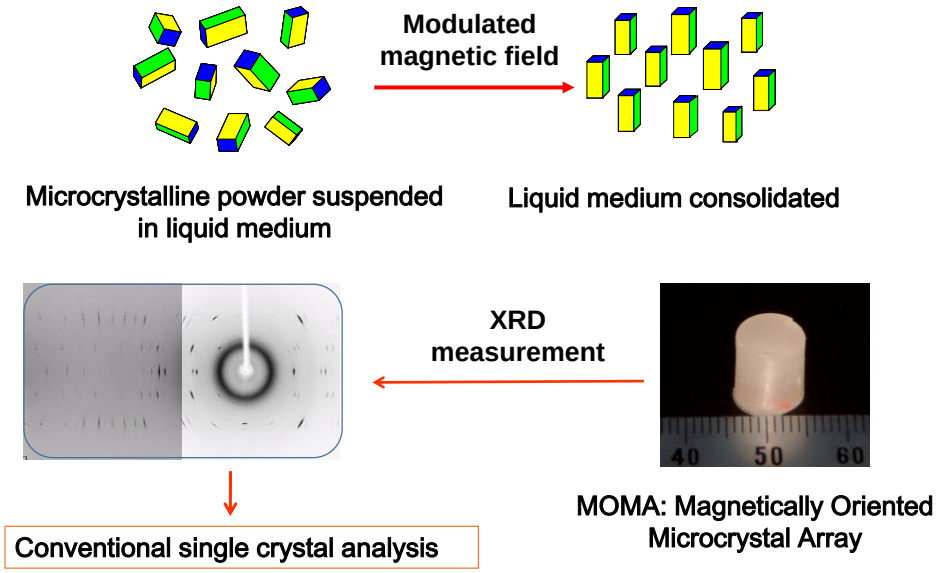

Fig. 1 Schematic of preparation of MOMA (magnetically oriented microcrystal array) and its X-ray diffraction from which the crystal structure is determined by using conventional single crystal analyses.