Emergence and Control of Crystal Chirality via Achiral Precursor in Sodium Chlorate Chiral Crystallization from Aqueous Solution

(溶液からの塩素酸ナトリウムキラル
結晶化におけるアキラルな前駆体を介したキラリティの発生と制御)

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Chiral symmetry breaking in chiral crystallization has significance from the viewpoint of the elucidation the origin of biohomochirality, chiral separation in pharmaceutical compounds and the control of the handedness in chiral magnetic materials for spintronic devices. Sodium chlorate (NaClO₃) crystallization from an aqueous solution is a typical example of chiral crystallization. Whereas a NaClO₃ aqueous solution is optically inactive, i.e. achiral, NaClO₃ crystal possesses chirality because of cubic chiral space group \( P2_13 \). Evaporation of static aqueous solution yields statistically equal numbers of both enantiomorphs. However, continuous stirring of the aqueous solution yields only either of the enantiomers. This significant chiral bias is called as “chiral symmetry breaking (CSB) in crystallization” and its mechanism still remains controversial. Despite of consensus view that transition towards homochiral state is achieved during the early stage of the crystallization actual emergence process of chirality which takes place during the early stage is still unclear, leading to the stereotypical view that the handedness of the crystal is determined before the primary nucleation stage. The aim of this study is to clarify the actual emergence process of chirality by means of direct \textit{in-situ} microscopic observation method and to control the chiral chirality on the basis of the knowledge obtained by the observation. These background and aims are described in the chapter 1.

The chapter 2 reveals the existence of unknown non-cubic crystal which appears prior to the formation of chiral cubic crystal by \textit{in-situ} polarized-light microscopic observation on the crystallization induced by droplet-evaporation method. Moreover, the observation also revealed that the unknown crystal transforms into the chiral crystal in accordance with Ostwald’s rule of stages.

The chapter 3 described structural analysis on the unknown crystal and solubility measurement to clarify whether the unknown crystal possess chirality or not and thermodynamic stability of the crystal, respectively. First, a cryogenic single-crystal XRD measurement, in which the unstable achiral crystal is maintained by being frozen throughout the measurement, was carried out. The measurement allowed us to determine crystal system, lattice constants, space group of the unknown phase as follows: monoclinic, \( a = 8.42(2), b = 5.260(7), c = 6.70(1) \ \text{Å}, \beta = 109.71(1)^\circ, \ \text{and} \ V = 279.8(8) \ \text{Å}^3 \), where \( V \) is the volume of the unit cell, \( P2_1/a \). It is noteworthy that the unknown phase belongs to achiral space group \( P2_1/a \). Comparing these crystallographic information and those of phase III, a metastable phase in NaClO₃ melt growth, they were found to be similar each other. Accordingly, the achiral monoclinic phase in solution growth was concluded to be identical to the phase III. Second, the solubility of the achiral crystal was successfully measured by overcoming instability of the crystal. Antisolvent crystallization method using acetone was found to selectively produce the achiral crystal usable as a seed crystal for the measurement. Using a
crystal fabricated by the method, the solubility was determined to be 1.6 times higher than that of the stable chiral crystal in the range from 10°C to 23°C. Therefore, the achiral monoclinic phase was proven to be a metastable phase in solution growth.

The chapter 4 provides in-situ microscopic observation with intensive attention to polymorphic transformation from the achiral crystal to the chiral crystal to investigate the emergence process of chirality. The observations revealed the emergence of chirality via two kinds of solid-solid polymorphic transformation (SSPT): (1) the one in which an achiral crystal directly transforms into a chiral crystal and (2) the one intermediated by a transient phase. It was implied that the deformation process of the SSPT(2) follows Meyer’s deformation model, which geometrically explains deformation from Phase III to chiral Phase I by two-step deformation process intermediated by achiral transient structure. Accordingly, crystal chirality emerges at the moment the transformation occurs in the SSPT of (1), whereas, chirality emerges at the moment the transient phase deforms in the SSPT of (2). The observations also observed the amplification of chirality via solvent-mediated phase transformation (SMPT), which is progressed by simultaneous dissolution of a metastable crystal with the growth of a stable crystal. It was revealed that when a chiral crystal approaches to an achiral crystal until their interfaces cannot be resolved by the microscope the achiral crystal instantly started to transform into a chiral crystal from the point at which the chiral crystal approached. This approach-facilitated SMPT certainly yielded the same enantiomorph as the enantiomorph that approached to the achiral crystal, implying the amplification of the same handedness by the approach-facilitated SMPT. This transformation was able to be rationalized by approach-induced transition of rate-controlling processes in SMPT, growth-controlled SMPT to dissolution-controlled SMPT.

The chapter 5 summarizes the observational facts and proposes the novel formation pathway of NaClO₃ chiral crystal intermediated by the achiral crystalline precursor. Additionally, this chapter also provides a novel scenario that explains the CSB from highly-s supersaturated aqueous solution, which cannot be explained by secondary nucleation scenario (SNS) proposed previously, on the basis of the novel pathway.

The chapter 6 demonstrated the possibility to control chirality of NaClO₃ crystal by means of non-photochemical laser-induced nucleation using circularly polarized light (CPL). It was achieved to induce the nucleation of an achiral crystal and its transformation by irradiation of tightly-focused CPL CW laser (λ = 532 nm) to the interface between air and unsaturated NaClO₃ aqueous solution in which Ag nanoparticle (d = 10 nm) dispersed. As a consequence, non-negligible chiral bias was observed in the probability of crystallization of enantiomorphs, showing the potential to control crystal chirality in chiral crystallization.

In conclusion, in this thesis, the author advocates that chirality of NaClO₃ chiral crystal emerges after the primary nucleation, that is, the crystal handedness is not determined at the primary nucleation stage (Newborn crystals are amibidextrous!) in contrast to the previous view that the handedness is already determined during pre-nucleation stage. The crystal handedness is determined through polymorphic transformations of achiral crystalline precursor to the chiral crystal. It was implied that the novel formation pathway of chiral crystal intermediated by an achiral crystalline precursor gives an explanation for the mechanism of the CSBs that cannot be explained by the previous view. Moreover, this study demonstrated that the possibility to control crystal chirality by inducing the achiral-chiral polymorphic transformation under strong CPL field.