

Emergence and Amplification of Chirality via Achiral-Chiral Polymorphic Transition in Sodium Chlorate Solution Growth

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Chirality is the concept that widely spreads in nature at various levels from elementary particles to morphology of plants. Although both the enantiomers have equal stability, lives on the earth preferentially selects one-type of the two enantiomers. This phenomenon is called homochirality, and its origin (the emergence of chirality) and the amplification of chirality are great puzzles in the evolution of life on the primitive earth. One candidate of the origin includes chiral crystallization of achiral compounds. Sodium chlorate (NaClO_3) undertakes chiral crystallization from achiral solution. NaClO_3 has chirality in its crystal structure due to the enantiomorphic space group of $P2_13$ (cubic). A *static* solution of the compound yields statistically equal numbers of the two enantiomorphs. However, Kondepudi *et al.* have strikingly revealed that a *stirred* solution yields only one-type of the enantiomorphs[1]. The mechanism of the significant chiral bias has not been elucidated. Diverse crystallization experiments have implied that the emergence and the amplification proceed during the early stage of crystallization. However, a direct investigation of the early stage is still missing. We therefore have carried out in-situ observations focusing on the early stage. The observations have revealed that achiral metastable crystals having $P2_1/a$ symmetry (monoclinic) appear prior to the formation of chiral crystals. The authors have reported this result in JpGU 2011[2]. Here, we present more detailed observations, and demonstrate that polymorphic transformation from the achiral phase to the chiral phase can be responsible for the emergence and the amplification.

A droplet (6 μl) of NaClO_3 aqueous solution saturated at 22 °C was put on a glass slide whose temperature is controlled at 22 °C by a Peltier device, allowing the droplet to evaporate isothermally. We observed crystallization process induced by the evaporation using a polarized light microscope. The microscope enables us to distinguish cubic crystals from non-cubic crystal by detecting birefringence, allowing us to distinguish chiral crystals from achiral crystals, and it can identify handedness of the chiral crystals by detecting optical rotation.

Polymorphic transformation from an achiral crystal to a chiral crystal was observed. The transformation could be classified into two kinds according to their transition rate. The slower one proceeds at 35 $\mu\text{m}/\text{sec}$ (Fig.A), and the faster did at 2000 $\mu\text{m}/\text{sec}$ (Fig.B). The slower transformation was induced by a contact with a chiral crystal. It is noteworthy that the resulting enantiomorph generated through the contact-induced transformation was certainly the same as the enantiomorph that contacted with the achiral crystal. The double digit difference in a rate of the two transformations is probably ascribed to difference in the mechanism, indicating the slower transformation and the fast one are solvent-mediated phase transformation (SMPT) and structural phase transition (SPT), respectively. The SPT probably generates both the enantiomorphs in equal probability since the activation energy required to transform should be equal. In contrast, the contact-induced SMPT preferentially generates the same enantiomorph as the contacted crystal. This inheritance of chirality through the contact-induced SMPT is possibly responsible for the amplification of chirality.

So far, the emergence and the amplification have been explained by primary nucleation of a chiral crystal and secondary nucleation from the crystal. In contrast, our observation provided a new sight based on the achiral-chiral polymorphic transformation: the emergence of chirality through the SPT and its amplification through the contact-induced SMPT.

References

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