粉砕や温度循環による結晶カイラリティの転換 Chirality Conversion of Crystals and Molecules by Grinding and by Temperature Cycling

Makio Uwaha¹ and Hiroyasu Katsuno²

¹Aichi Institute of Technology, Toyota, Japan (email: uwaha@nagoya-u.jp) ²Department of Physical Sciences, Ritsumeikan University, Kusatsu, Japan

Finding mechanisms of symmetry breaking in nature such as the broken chiral symmetry of amino acids and sugars in a living body is a big challenge. It may be related to simple chemical or physical processes that give rise to homochiral states. Controlling the molecular chirality is crucial in pharmaceutical engineering. It was found that chirality of crystal structure can be converted by simple grinding to realize a homochiral state[1]. The method was applied to crystals of chiral molecules that form conglomerate so that the chirality of molecules can be converted simultaneously[2].

These surprising nonequilibrium phenomena can be explained by taking account of chiral clusters in the process of crystal growth[3]. The basic idea is incorporation of chiral clusters, which are overproduced by grinding, to relatively large crystals of the same chirality, as schematically depicted in Fig.1. This scheme assumes a steady size distribution of crystals, which has been confirmed by the use of a generalized Becker-Döring model[4]. Although the experiment is simple, to confirm the above key mechanism experimentally is very difficult.

More recently, a similar phenomenon, chirality conversion of crystals and molecules, without grinding was found experimentally[5]. By changing periodically the temperature of a solution containing powder crystals of both chirality, it is possible to obtain crystals of a single chrality. The temperature cycling converts the minority species into the majority. We have succeeded to reproduce the chirality conversion with a similar statistical model based on the same cluster incorporation mechanism[6]. The chiral clusters act as a reservoir and pump out the minority to the majority.

In all cases the key factor that realizes the exponential amplification of an initial enantiomeric excess to the homochiral state is the acceleration of crystal growth with chiral clusters.

We will also report recent development on the anomalous change of the cluster size distribution during the chirality conversion by grinding with ultrasound.



Figure 1: Schematic model of cluster incorporation to crystals. X, Y: chiral crystals. X_u, Y_u : chiral clusters, Z: achiral monomers.

References

- [1] C. Viedma, Phys. Rev. Lett. **94**, 065504 (2005).
- [2] W. L. Noorduin *et al.*, J. Am. Chem. Soc. **130**, 1158 (2008).
- [3] M. Uwaha, J. Phys. Soc. Jpn. 73, 2601 (2004); 77, 083802 (2008).
- [4] M. Uwaha and H. Katsuno, J. Phys. Soc. Jpn., 78, 023601 (2009).
- [5] K. Suwannasang, A. E. Flood, C. Rougeot, and G. Coquerel, Cryst. Growth Des. 13, 3498 (2013).
- [6] H. Katsuno and M. Uwaha, Phys. Rev. E 93, 013002 (2016).