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the Mechanism of Emergence of Chirality in $NaClO_3$ Crystals from a Solution

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Chiral symmetry breaking in sodium chlorate ($NaClO_3$) crystallization from a solution was reported by Kondepudi et al.(1990)[1]. The chiral $NaClO_3$ crystal is cubic, and its space group is $P2_13$. When $NaClO_3$ crystals crystallized from a static solution by evaporation, equal numbers of L-crystals and D-crystals appeared. In contrast, from a stirred solution, almost only one type of crystals appeared. This significant bias of chirality is termed as chiral symmetry breaking. Although there are some theories about the process that causes the chiral symmetry breaking, the real process has not been elucidated yet. To obtain the direct evidence of chirality symmetry breaking, we carried out in-situ observation of crystallization process from a $NaClO_3$ solution by polarization microscope. As a result of the observation, it was found that non-cubic metastable crystals appeared from the solution at first, and then, the crystals transformed to cubic crystals by a solid-solid phase transition or a solution-mediated phase transition [2].

If the metastable crystal does not have chirality, it can be said that chirality of the cubic crystal emerges when the phase transition occurs. However, since the structural analysis of the metastable crystal has not been carried out, it is not clear whether the metastable crystal has chirality or not. It is important to clarify the crystal structure of the metastable crystal for a new understanding of chiral symmetry breaking in the $NaClO_3$ solution.

The object of this study is to clarify the mechanism of chiral symmetry breaking in a $NaClO_3$ solution by measuring the crystal structure of the metastable phase by means of single-crystal X-ray diffraction experiment.

The metastable crystal was prepared by drop evaporation method as follows. A drop (6 microliter) of a $NaClO_3$ solution saturated at room temperature(293K) was put onto a cover glass. The metastable phase crystallized out in the drop as the solution evaporated. After the crystal grew up to 200 micrometer in size, we replaced the drop with glycerin. At the end, the crystal and the drop of glycerin were frozen by liquid nitrogen. The frozen drop is the specimen for the X-ray diffraction analysis. We used Imaging plate type single-crystal X-ray diffractometer (R-AXIS IV++, Rigaku). To keep specimen frozen during the analysis, temperature around the specimen was kept at -266$_-^+$1(K) by Cryostream (Oxford). Analytical method is the oscillation method.

As a result, we determined the lattice constant, crystal system and space group of the metastable phase as follows; a=8.42 (A), b=5.26 (A), c=6.70 (A), *beta angle*=109.71^o, monoclinic, and $P2_1/a$, respectively. These values are very similar to that of $NaClO_3$(I), which is high temperature phase of $NaClO_3$ crystal in melt growth (a=8.78 (A), b=5.17 (A), c=6.83 (A), *beta angle*=110^o, monoclinic, and $P2_1/a$) [3]. Therefore, it is highly possible that the metastable phase is the same as the $NaClO_3$(I) phase. In addition, a crystal having a space group of $P2_1/a$ does not have chirality, that is to say, the metastable phase that we obtained from the solution does not have chirality. From these results, we concluded that chirality of the cubic $NaClO_3$ crystal emerges when the phase transition occurs.

In this study, we revealed that the metastable phase of $NaClO_3$ crystal in solution growth does not have chirality. It also becomes clear that chirality of a cubic crystal emerges when the solid-solid phase transition occurs.

References

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