

in-situ observation of NaClO₃ crystal growth -discovery of a precursor of chiral crystals-

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The crystal of sodium chlorate (NaClO₃), of which crystal system is cubic, has chiral structure. When we crystallize NaClO₃ from a static solution, we can get equal numbers of L- and D- types of crystals. In contrast, from a stirred solution, we can get almost only one type of crystals (Kondepudi et al., 1990). This phenomenon is referred as chiral symmetry breaking. Although there are several theories about processes which cause chiral symmetry breaking, the real process has not been understood yet. One reason is lack information relating this crystallization process such as in-situ observation. In addition, it is not known when chirality of the crystal is determined during the crystal growth.

Therefore, we focus on the process of chiral symmetry breaking and study the process which determines chirality of the crystal by means of microscopic in-situ observation. As a result of the observation, we discovered a precursor of chiral NaClO₃ crystals.

The experimental scheme is following. We prepare a NaClO₃ solution saturated at 343.15(k), and then put a drop (3 micro l) of the solution on a slide glass. The temperature of the slide glass is adjusted at about 283.15(k) by a Peltier device. The drop becomes supersaturated as it cools down and crystallization occurs in it. We observed the crystallization process in the drop by a polarized microscope, which can distinguish chirality of these crystals in-situ.

At the initial stage of the crystallization, parallelogram crystals appear in the drop. They are much brighter than ordinary cubic chiral crystals under crossed nicol. In addition, the bright crystals have extinction positions. In general, a cubic crystal looks dark under crossed nicol, and does not have extinction positions. Therefore, the bright crystal is not the chiral cubic crystal observed in previous chiral breaking experiments. We refer the bright crystal as an optically anisotropic crystal hereinafter. After that, some of the optically anisotropic crystals changed to crystals which were dark under crossed nicol. The dark crystal did not have extinction positions. Hence, it is considered as the cubic NaClO₃ crystal. Our observations clearly show that the chiral cubic NaClO₃ crystals have been formed from the optically anisotropic crystals by a phase transition.

When optically anisotropic crystals contacted with a cubic crystal, they transformed to cubic crystals, and the transformation started from the contact point. Then, chirality of the transformed cubic crystal is the same as that of the cubic crystal which contacted.

It was also observed that an optically anisotropic single crystal transformed to two cubic crystals of different chiralities when the transformation has started from two separate points.

The optical property that the optically anisotropic crystal is extremely bright under crossed nicol originates from birefringence. The crystal which have birefringence are classified to two types; optically uniaxial crystals or optically biaxial crystals. Assuming that the most developed face of the optically anisotropic crystal is a C face, we may conclude that the crystal is optically biaxial; because when we observe a C face of an optically uniaxial crystal in crossed nicol, birefringence should not be seen. The crystal systems which show the optical biaxial property are triclinic, monoclinic, and orthorhombic. Among them, the crystal system whose C face is parallelogram is only triclinic. Therefore, crystal system of the optically anisotropic crystal is most likely triclinic. From this observation, we conclude that in NaClO₃ crystal growth, triclinic crystals crystallize first,

then the triclinic crystal transforms to a cubic crystal by a phase transition. We also think that chirality of the NaClO_3 crystal is determined when the phase transition occurs. The phase transition triggered by the triclinic-cubic contact may cause the macroscopic chiral symmetry breaking.