Imaging chirality-domain morphology in racemic mixed crystal of CsCuCl$_3$

Chirality is the property of having non-superimposable mirror images such as human hands. Since molecular handedness determines biological activity, discrimination of molecular handedness is indispensable for drugs used in medicines, food additives, and so forth. Hence, the handedness-selective synthesis of molecule-based materials has been extensively studied and become a common practice. On the other hand, the chiral crystallization of non-molecular materials is attracting considerable attention as a method for obtaining potential materials for spintronics because a non-centrosymmetric electrostatic potential induces Rashba-type spin-orbit coupling or the Dzyaloshinskii-Moriya interaction. However, no universal guiding principles exist for growing a single-handed crystal consisting of achiral atomic components.

Interpretation of the chirality-domain morphology is essential for finding key factors controlling the handedness of an atomic arrangement and for establishing regulations for single-handed crystal growth. However, there is no appropriate technique for observing the chirality-domain morphology. In contrast to that observed in an aqueous solution, optical rotation also arises from crystal anisotropy (linear birefringence), which obscures the chiral effect (circular birefringence). Owing to Friedel’s law, diffraction experiments are also not suitable for the discrimination of handedness in an atomic arrangement. However, the X-ray screw-axis ATS reflection (here, ATS represents the anisotropy of the tensor of susceptibility) may enable us to discriminate crystal handedness [1]. Near X-ray absorption edges, the intensity of the reflection depends on the handedness of both the atomic arrangement and the circular polarization. Thus, one can examine crystal handedness by measuring the flipping ratio and the namely, difference-over-sum ratio between reflection intensities for right- and left-handed circularly polarized incident X-rays [2]. Dark-field scanning X-ray microscopy with the screw-axis ATS reflection and a depth-profiling technique allow us to reconstruct a three-dimensional image of the chirality-domain distribution [3].

A schematic of the chirality-domain imaging experiment at beamline BL39XU is shown in Fig. 1. Linearly polarized X-rays from a planar undulator were converted to circularly polarized X-rays by using a diamond phase retarder. Kirkpatrick-Baez (KB) mirrors focused the circularly polarized X-ray beam to $2.7 \times 2.7 \mu m^2$ at the sample position. A cleaved (001) CsCuCl$_3$ surface was raster-scanned and the flipping ratio of the screw-axis ATS reflection 00/ ($l = 14$) at each point was measured to construct an image of the chirality-domain distribution. CsCuCl$_3$ is a hexagonal perovskite system belonging to a chiral space group of $P6_{1}22$ or $P6_{5}22$ (Fig. 2) and crystallizes as a racemic mixed crystal from an aqueous solution. The obtained raster image of the flipping ratio revealed that the typical chirality-domain size was several tens of microns in the lateral direction. To realize three-dimensional imaging, we have developed the new nondestructive depth profiling technique shown below.

The penetration depth of X-rays varies with the photon energy especially near absorption edges. Figure 3(a) shows the penetration depth for the Bragg condition of the 001 ($l = 14$) reflection around the Cu K-edge. Flipping ratio maps of the same area, which are shown as top surfaces in Figs. 3(b)–3(e), were measured with X-rays having various photon energies of (b) 8.992 keV, (c) 8.987 keV, (d) 8.985 keV, and (e) 8.984 keV. Differences among them are attributed to the variation in penetration depth, from which one can determine the depth profile of handedness in an atomic arrangement. The reconstructed three-dimensional image of the

![Fig. 1. Schematic of chirality-domain imaging experiment on a CsCuCl$_3$ racemic mixed crystal. An X-ray phase plate converted linear polarization to circular polarizations. KB mirrors focused a circularly polarized X-ray beam on the sample. The sample surface was raster-scanned through the beam.](image-url)
chirality-domain distribution revealed the following morphological features in CsCuCl$_3$: a chirality-domain boundary is preferentially formed parallel to the hexagonal $c$-plane; the typical domain is only a few microns thick with a size of several tens of microns in the lateral direction. The observed shallow chirality-domain shape suggests that relatively high in-plane cooperativity of the Jahn-Teller distortion of CuCl$_6$ octahedra is the predominant factor that determines the chirality-domain morphology in this material. This three-dimensional imaging technique facilitates the observation of the chirality-domain morphology and the understanding of the underlying twinning mechanisms, which will provide support to the increasing demand for improvement of the inorganic chiral crystal engineering.

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