

Crystal Growth of Chiral Magnetic Material in CsCuCl_3

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Abstract. We report a crystallization technique to make single crystals with homochiral crystallographic domain in CsCuCl_3 . By adapting crystallization technique with stirring, we succeeded in obtaining the mm-ordered enantiopure single crystals. The samples obtained without the stirring crystallization technique had zigzag shape, suggesting many crystalline nuclei combined during the crystallization process. The samples done with the stirring crystallization technique formed quart-crystal-like shape, suggesting only one crystalline nucleus grew. Absolute structure analysis using X-ray diffraction showed that the samples grown only by our technique had a homochiral crystalline domain.

1. Introduction

Chirality concept (right-handedness or left-handedness) is one of the most fundamental building blocks of nature, ranging from nano and biosciences to cosmic sciences. Therefore, it is very important to understand the chirality in molecules, crystals and magnetic structures both from theoretical and experimental viewpoints. Recently, the interplay between crystallographic and magnetic chiralities have been paid attention because the properties of a helical magnetic structure (pitch, sense, etc..) strongly depends on the chiral skeleton structure that could allow an antisymmetric Dzyaloshinskii-Moriya (DM) interaction [1, 2]. In inorganic compounds, it is still a big challenge to control the crystallographic chirality. Transition-metal monosilicides with B20 type chiral crystal structure are a unique example to form homochiral crystal structure [3]. The magnetic chirality follows the crystalline chirality [4]. By use of conventional spontaneous crystallization technique, a water-soluble B20 type compound NaClO_3 forms racemic-twinned crystals, containing the left- and right-handed crystalline domains in a crystalline sample. With stirring the solution during the crystallization process, crystalline specimen can be a homochiral domain [5]. However, in case of most of the inorganic magnetic materials, single crystalline samples form racemic-twinned crystals.

CsCuCl_3 has a chiral crystal structure with chiral space groups of right-handed $P6_122$ or left-handed $P6_522$. The crystal structures are shown in Figure 1. Quasi-one-dimensional chains of Cu^{2+} ions form right- or left-handed helices with a period of six ions along the c -axis. The DM vector is along the c -



axis. Magnetization measurements show an antiferromagnetic response at $T_N = 10.5$ K. Cooling temperature below T_N , unpolarized neutron diffraction studies show helimagnetic ordering with the magnetic propagation vector $\mathbf{k}_{mag} = (1/3, 1/3, \pm\delta)$ [6].

Crystallographic chirality is generally determined by an absolute structure analysis. The intensities of a pair of reflections at (h, k, l) and $(-h, -k, -l)$, termed Bijvoet pairs, are not equivalent because atomic scattering amplitude in X-ray diffraction includes imaginary part, called anomalous scattering [7]. Flack parameter x can be obtained as a fitting parameter of the structure analysis, which is expressed as $I_{obs} = (1-x)I_{cal}(h, k, l) + xI_{cal}(-h, -k, -l)$ [8, 9]. Here, I_{obs} and I_{cal} are the observed and calculated intensities, respectively. We have synthesized single crystals of CsCuCl_3 and evaluated the crystallographic chirality using circularly-polarized resonant X-ray diffraction [10, 11]. Our findings indicate that mm-ordered single crystalline samples grown by conventional crystallization technique form only racemic twinned. The domain sizes of the left- and right-handed chiralities are tens of micrometers. To make a homochiral domain in CsCuCl_3 , we report a crystallization technique as spontaneous crystallization with stirring.

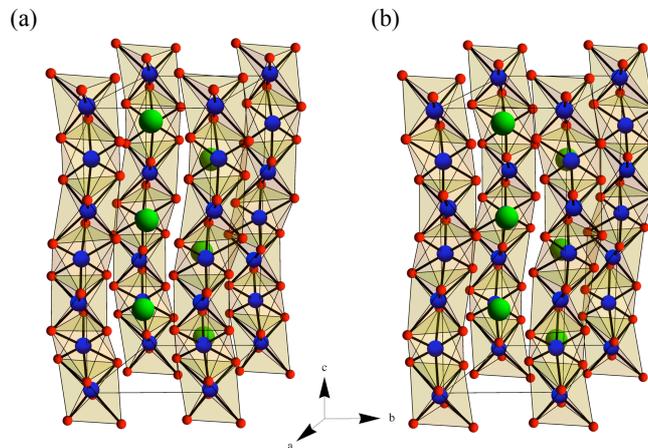


Figure 1. (Color online) Crystal structures of (a) right-handed (space group: $P6_122$) and (b) left-handed (space group: $P6_522$) CsCuCl_3 . Large, middle and small balls represent Cs, Cu and Cl ions, respectively.

2. Experiments

Single crystals of CsCuCl_3 were prepared from an aqueous solution containing CsCl and CuCl_2 by slow evaporation of a slightly acidified solution. To avoid the undesired formation of Cs_2CuCl_4 , the CuCl_2 content of the solution was increased by 10 % from the stoichiometric composition. Firstly 40 ml CsCuCl_3 solution was prepared in 100 ml beaker. During the crystallization process, we constantly stirred the solution using Teflon stirrer-bar with the size of 8 mm diameter and 35 mm length. To prevent dust particles from entering the solution, we covered the beakers with a tissue paper. To evaluate the validity of the stirring, we also grow single crystals without stirring.

By optimizing the speed of stirring and cooling temperature, we succeeded in obtaining hundreds of single crystals from a beaker with the size of 0.4 ~ 1.0 mm diameter and 1 ~ 3 mm length. To evaluate the crystallographic chirality of the obtained crystals, X-ray oscillation photographs were taken at 300 K on a Bruker APEX II area detector using $\text{Mo } K\alpha$ radiation. With applying empirical absorption correction to the observed intensity, the absolute structures were solved by direct methods and refined using the SHELXS-97 software package [12]. The chiral crystal structures were evaluated by the refined Flack parameters. Racemic twinned crystals have Flack parameter = 0.5. The right-handed crystals have Flack parameter = 0 by assuming the space group of $P6_122$, and the left-handed crystals have Flack parameter = 0 by assuming the space group of $P6_522$. Due to the limitation of the X-ray beam diameter, the diameter of all the checked samples was smaller than the beam diameter. And, to evaluate the chirality of a whole sample, we obtained the data from end to end of the sample

with the step of 0.7 mm along the length direction, and evaluated Flack parameters at each radiated position. In total, we checked 80 pieces of the crystalline samples with the average size of 0.7 mm diameter and 2.5 mm length.

3. Results

Figure 2 shows pictures of single crystals obtained by conventional crystallization technique without stirring and by our method with stirring. The samples obtained without stirring look zigzag shape, and the samples done with stirring look quart-crystal-like shape.

Absolute structure analysis showed that all the samples crystallized without stirring were racemic twinned crystals with Flack parameter ~ 0.5 . On the other hand, the samples crystallized with stirring formed single crystalline chirality domain with Flack parameter ~ 0 . As an example, Table 1 shows the results of the absolute structure analysis obtained by a sample crystallized with stirring or without stirring. Flack parameters were determined by assuming the left-handed space group of $P6_522$. Both samples have the same atomic positions except for Flack parameters. While the sample crystallized without stirring forms racemic twinned crystal with Flack parameter ~ 0.5 , the sample done with stirring forms the right-handed homochiral structure with Flack parameter ~ 0 . We note that the samples obtained with stirring can be categorized to 3 types, having only the right-handed, only the left-handed and both-handed domains. The samples having both-handed domains formed only the left-handed domain in one end, and the right-handed in the other end. Although Flack parameters at the both end of the sample were zero, the both-handed samples can be regarded as racemic twinned crystals. Table 2 shows the number of each type of the crystals obtained from a breaker. The number of left- and right-handed enantiopure crystals was nearly the same. And we can see some of the both-handed crystals. Therefore, we can conclude that the left- and right-handed crystals are energetically degenerated in a breaker.

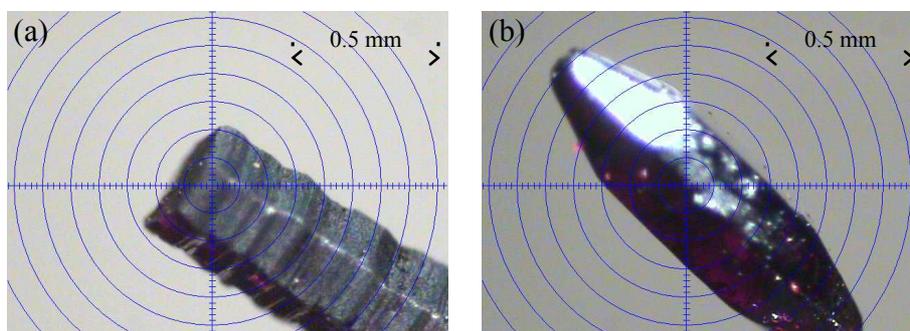


Figure 2. (Color online) Photographs of single crystalline CsCuCl_3 , obtained by spontaneous crystallization (a) without stirring (conventional method) and (b) with stirring (our method).

Table 1. Results of absolute structure analysis obtained by single crystalline X-ray diffraction. The data was taken at one end of a sample crystallized with or without stirring the solution. Flack parameters were determined by assuming the space group of $P6_522$

Crystallization method	R	wR	Flack parameter
Without stirring	0.0330	0.0690	0.49(5)
With stirring	0.0305	0.0694	0.06(5)

Table 2. The number of each type of samples crystallized with stirring obtained from a breaker. See text for the definition of the types.

Left-handed	Both-handed	Right-handed
31	22	27

4. Discussion

To obtain enantiopure single crystals by use of conventional crystallization method without stirring the solution, we previously reported that maximum size of sample must be submillimeter-ordered [10]. Our stirring crystallization technique obviously enlarges the size of enantiopure domains, and obtains mm-ordered homochiral samples.

The circularly-polarized resonant X-ray micro diffraction indicates that the size of each homochiral domain in the racemic twined CsCuCl_3 is tens of micrometers [11]. In case of conventional crystallization process without stirring, many crystalline nuclei grow to tens of micrometers and then combined to one crystal. Therefore, the zigzag shape of the sample suggests the existence of several crystalline nuclei in a sample. On the other hand, the quartz-crystal-like shape samples done with our stirring technique indicates only one crystalline nucleus grew to mm-ordered single crystals. It suggests that the aqueous stream due to stirring prevents each growing nucleus from combining during the crystallization process. Obtaining some of the both-handed crystals indicates that two pieces of the mm-ordered homochiral crystals can be merged to one crystal. Therefore, the present amplitude of the water flow cannot avoid combining some of the growing nuclei completely. Kondepudi reported that most of obtained NaClO_3 samples crystallized with stirring in a breaker were only left- or right-handed. With several crystallizations obtained by different breakers, the number of left- and right-handed crystals finally becomes the same [5]. This behavior is different from ours because we obtained equal number of the left- and right-handed crystals in a beaker.

In summary, we succeeded in obtaining the mm-ordered enantiopure single crystals of CsCuCl_3 by adapting crystallization technique with stirring solution. The mm-ordered enantiopure chiral magnetic crystals enable us to perform a variety of experiments for investigating the interplay between crystalline and magnetic chirality.

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