Journal of Crystal Growth 312 (2010) 3243–3246

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth of $(CH_3)_2NH_2CuCl_3$ single crystals using evaporation method with different temperatures and solvents

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ARTICLE INFO

Article history:
Received 1 June 2010
Received in revised form
17 July 2010
Accepted 25 July 2010
Communicated by M. Roth
Available online 1 August 2010

Keywords:
A1. X-ray diffraction
A1. Recrystallization
A2. Growth temperature
A2. Solvent

ABSTRACT

The bulk single crystals of low-dimensional magnet $(CH_3)_2NH_2CuCl_3$ ($DMACuCl_3$ or MCCL) are grown by a slow evaporation method with different kinds of solvents, different degrees of super-saturation of solution and different temperatures of solution, respectively. Among three kinds of solvent, methanol, alcohol and water, alcohol is found to be the best one for growing MCCL crystals because of its structural similarity to the raw materials and suitable evaporation rate. The best growth temperature is in the vicinity of 35 °C. The problem of the crystals deliquescing in air has been solved through recrystallization process. The crystals are characterized by means of X-ray diffraction, specific heat and magnetic susceptibility.

1. Introduction

Catena (dimethylammonium-bis(μ_2–chloro)-chlorocuprate) $(CH_3)_2NH_2CuCl_3$ ($DMACuCl_3$ or MCCL) is an organic-metallic magnetic material with quasi-one-dimensional alternating antiferromagnetic–ferromagnetic (AFM–FM) Heisenberg chain ($S=1/2$). MCCL is very interesting in the regard that it has a rather complex $H-T$ phase diagram and multiple magnetic-field-induced phase transitions. Willett first proposed that Cu^{2+} ions ($S=1/2$) coupled via Cu-halide-Cu bridges to form magnetic chains along the crystallographic a axis, but Stone et al. recently found that there was a significant dispersion along the b axis by inelastic neutron scattering, indicating that the b axis is the one-dimensional magnetic axis [1–4]. It is found that the magnetization shows a 1/2 plateau, corresponding to a field-induced gapped state, with magnetic field range from 2 to 3.5 T [5]. There are a spontaneous AFM ordering and a field-induced one below and above the plateau, respectively [6,7]. It would be very useful for studying the mechanisms of these magnetic transitions if one can get high-quality single crystals of MCCL.

A slow evaporation method using water, methanol or alcohol as a solvent was originally introduced in 1960's to grow MCCL crystals [1]. Recently, several groups also obtained MCCL crystals, including the deuterated crystals, by using Willett's method [2,3,5–7]. However, the conditions of the crystal growth, the sizes and the quality of the obtained crystals are not clearly mentioned in these papers. It is therefore still important to investigate the appropriate growth procedure. In this work, we report a detailed study on the MCCL crystal growth using this method. It is found that the MCCL single crystals can be synthesized in different kinds of solvents, including methanol, alcohol and water. The sizes and the shapes of the crystals, however, are dependent not only on the type of solvent but also on the degree of super-saturation of solution and the growing temperature. The biggest crystal with size of $12\times7\times4\,mm^3$ is obtained from 100 ml alcohol solution (containing raw materials of 15 mmol $CuCl_2\cdot2H_2O$ and 15 mmol $(CH_3)_2NH_2Cl$) at 35 °C. A common problem of the crystal deliquescing in air can be overcome by using a recrystallization process.

2. Crystal growth

$(CH_3)_2NH_2Cl$ and $CuCl_2\cdot2H_2O$ in the molar ratio 1:1 are used as the starting materials for synthesizing MCCL. The chemical reaction formula between the two raw materials is

$$(CH_3)_2NH_2Cl+CuCl_2\cdot2H_2O\rightarrow(CH_3)_2NH_2CuCl_3+H_2O.$$

At first, 15 mmol $CuCl_2\cdot2H_2O$ is dissolved in a selected solvent (methanol, water or alcohol) at different temperatures. Then, the same mole amount of $(CH_3)_2NH_2Cl$ is added to the solution slowly with continuously stirring. Keeping the solution in the super-saturation state, then the crystals can grow gradually with the solution continuously evaporating.

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doi:10.1016/j.jcrysgro.2010.07.055

Table 1
Results for different growth temperatures in 150 ml solvent of water.

Temperature (°C)	Crystal state
20	Big bright pieces, size about (5–9) × (3–5) mm^2
35	Bright tiny slice
40	None
50	None

Table 2
Results for different growth temperatures in 150 ml solvent of alcohol.

Temperature (°C)	Crystal state
20	Flat crystal, but poor quality
35	High-quality crystals, size about (3–7) × (2–3) × (2–4) mm^2
40	None
50	None

Table 3
Results for different growth temperatures and different volumes for methanol solvent.

Volume (ml)	Temperature (°C)	Crystal state
60	20	Thin bright pieces, size about (4–7) × (2–3) mm^2
70	20	Small crystals, size is (0.5–2) × (0.3–1) × (0.1–0.8) mm^2
150	20	Bright thin pieces, size about 5 × 4 mm^2
150	35	None
150	35	None
150	40	None
150	50	None

The amount of starting raw materials is 15 mmol.

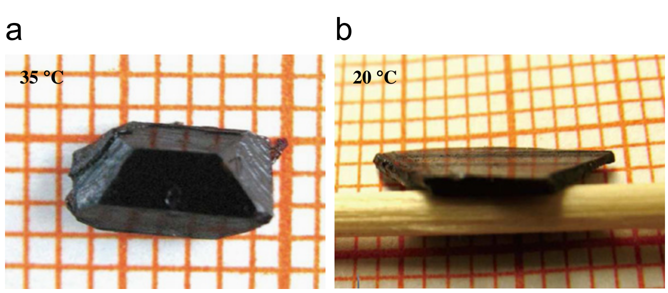

Fig. 1. The crystals grown at different temperatures in alcohol. They have very different shapes. In panel (a), the irregular crystal has four bright planes and good quality. In panel (b), the flat crystal has a big shining plane but poor quality.

We study the influence of the temperature on the crystal growth under the condition that both the amount of raw material and the degree of super-saturation solution are invariant. The volumes of solvents are chosen to be 150 ml. For aqueous solvent, the solution evaporates too fast to form single crystals at temperatures above 50 °C, while we can obtain shining tiny slice-like crystals and big crystals with thin smooth surface at 35 and 20 °C, respectively. In addition, the solution at 20 °C evaporates very slowly and it takes a very long time (about three months) to get crystals. These results are listed in Table 1. The similar investigations and results by using alcohol as the solvent are given in Table 2. There are no crystals at temperatures above 40 °C; while many high-quality single crystals with typical size of (3–7) × (2–3) × (2–4) mm^3 can be obtained after one week at 35 ± 2 °C. If we keep the growing temperature at 20 °C, the obtained crystals have considerably big sizes but poor quality, checked by the X-ray diffraction (XRD). For methanol solvent, there are no any high-quality single crystals though we make many attempts, see results in Table 3. From the above, there is notable difference among the results of three solvents at the same growth temperatures. The main reason is that the ability of crystal growth may strongly depend on the similarity of structure between the solute and the solvent. Another possible reason is that the different solvent molecules have different adsorption choices to the faces of the crystals, leading to different growth rates of the crystallographic planes and consequently forming different shapes of the crystals [8–10]. Moreover, the growth temperatures have significant effect on the quality and shape of crystals even in the same solvent. Fig. 1 shows the shapes of MCCL crystals grown at different temperatures in alcohol. The temperature can be considered as an activation energy to affect the processes of the crystal growth, which is either a pure surface reaction process or a pure diffusion process. In general, the surface reaction of the crystallization process plays the main role at low temperature. When the temperature rises, the growth rate becomes faster and the diffusion process will gradually dominate the growth of the crystals. The crystals grown at an appropriate higher temperature usually has better quality than those grown at low temperature (but too high temperature causes too fast evaporation to generate crystals), because the driving force of the crystallization, which is the ability of crystallized particles rejecting impurities, is enhanced with increasing temperature [11]. Generally, the sample has a flat irregular shape and normally grows with the (1 1 0),(0 1 1) and (0 0 1) planes developed. The largest crystal face is the (1 1 0) plane.

One problem we meet is that the MCCL single crystals deliquesce in air so easily that they can completely be destroyed after keeping in air for two days, which makes both the sample preservation and the measurement very difficult. We adopt the

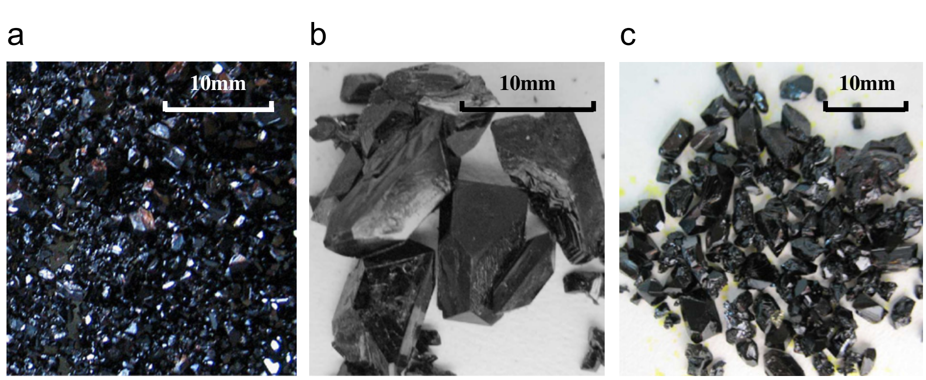

Fig. 2. Crystals grown from alcohol solvent at 35 °C with different amounts of solvent. The 15 mmol of each raw material is dissolved in 80, 100 and 150 ml alcohol, respectively.