Growth of Delafossite $CuCr_{1-x}M_xO_2$ Systems and Their Anisotropic Magnetization

M. Diantoro*
Department of Physics, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145 Indonesia

A. A. Nugroho
Department of Physics, Institute Teknologi Bandung, Jl. Ganesha 10 Bandung Indonesia

J. Baas, G. Blake, and T. T. M. Palstra
Solid State Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract

The effort to obtain a good crystalline state of delafossite $CuCrO_2$ phase is becoming important along with their potential application and scientific important results. In this paper we report the result of crystal growth and their Magnetic and Electric Capacitance Measurements. We focused on two methods i.e. flux decomposition (FD), and $Bi_2O_3$ Flux Growth (FB). The starting materials for FD growth were $K_2Cr_2O_7$ and CuO taking the advantage of the potassium dichromate’s decomposition. In case of FB flux growth, we should prepare the correct molar ratio for $CuCrO_2$ pellet on the $Bi_2O_3$ powder in 1 : 6 ratio. It is found that both methods are possible to obtain crystalline phases along with their specific technical processes to be overcomed. We show that FB method resulted flaky shapes while FD method produced rather bulky morphology. The obtained samples were checked by CAD4 single crystal diffractometer for their lattices and MPMS-SQUID magnetometer for their magnetization for different orientation. We check also the electric capacitance at the range of 5 K to 300 K along with their specific technical processes to be overcomed. It is found that their single Neel temperature ($T_N$) fall around 25 K. A distinct anisotropy of magnetization profiles shown by its crystal directions and planes. On the other hand the out of plane electric capacitance of Mn doped crystal did not show any transition at the range of 5 K to 300 K.

Keywords: Delafossite, $CuCrO_2$, flux decomposition, Bismuth flux, anisotropy magnetization

I. INTRODUCTION

Recently transparent conducting oxides (TCO) are becoming increasingly studied due to their potential application as well as their scientific interest. TCOs are critical components in flat panel displays, photovoltaic cells, low-emitting windows and organic optoelectronic devices. The current TCO industry is dominated by just few materials such as ITO (Indium Tin Oxide) or ZnO, being exclusively n-type conductors [1]. However, the lack of p-type TCOs limits their potential application in optoelectronic devices operating in the ultraviolet-blue region [2].

The delafossite compound is one of system that possessing an attractive high temperature electronic semiconducting properties. Many effort has been focused on improving the transparency and conductivity of p-type TCO thin film. Substituting the trivalent site of M by divalent ions induce hole into the system. Some of divalent are Ni$^{2+}$, Mn$^{2+}$, Mg$^{2+}$ [3, 4], Ca$^{2+}$ and Zn$^{2+}$ [5] make it possible to control their properties.

This system has also shows a triangular spin lattice antiferromagnetic (TLA) having ordered Neel temperature $T_N$ around 24 K. At medium to high temperature range this compound fit to Currie-Weiss formula. It has been reported that this $CuCrO_2$ single crystal shown a lower $T_{N1}$ at 23.6 K and higher $T_{N2}$ at 24.2 K [6]. These two $T_N$’s (Fig. 2) were obtained by measuring magnetization in plane and along c respectively. Typical E-P hysteresis below $T_N$ also shown by the crystal as illustrated in Fig. 2. Spin chirality, i.e., handedness of an ordered magnetic state, in frustrated magnets showing noncollinear spin structure, has been extensively discussed because it has been theoretically predicted to play an important role in magnetic ordering of frustrated systems, such as spin glasses and spiral magnets. However, it is not straightforward to However, these studies have not yet been fully substantiated owing to limitation of experimental facilities and requirement of a large single crystal. Our target in the present work is focused on preparing single crystals by means of flux decomposition and flux using $Bi_2O_3$ and temperature induced magnetization at different orientations.

II. EXPERIMENTAL

Prior to grow the $CuCr_{1-x}M_xO_2$ delafossite systems by means of FD and FB Flux growths, we firstly check the possible single phase of formation. The polycrystalline samples were prepared using a conventional solid state reaction. An appropriate composition of $Cu_2O$, $Cr_2O_3$, for pure and ei-
ther MnCO$_3$ or MgO as a dopant then mixed and ground thoroughly and sintered at 1200°C for 24 hours interfered by intermediate grinding and calcined at 825°C for 12 hours. Details of the preparation has been published elswhere. A fine mixture grains of pure and doped CuCrO$_2$ (CCO) were examined using D8-Bruker at 7 seconds per step with 0.02 degrees increments using CuK$\alpha$ wavelentgh.

In principle we used a method proposed by Ye et.al [7] of CuCrO$_2$ delafossite crystal growth. The raw material were prepared starting from CuO and potassium dichromate K$_2$Cr$_2$O$_7$ with ratio of 1 : 1. The raw materials were ground using agate ball millinge machine of Pulverizette 6 around 4 hours at 150 rpm. Other samples prepared with and without pressed in pellet after grinding. We tried also immersed seeds of small crystalline CuCrO$_2$ from previous results. The prepared samples were mounted inside Pt or Pt/Rh crucibles as depicted in Figure 2.

Samples firstly heated at rate of about 50 - 100 hours per minutes to totally melt (TL) at 850 °C to 900°C then soaked around 10 to 24 hours, hit quenched to 835°C to 875°C (C) to D 825°C about 50 to 80 hours then to E ( 810°C - 820°C) around 12 to 24 hours following by furnace cooling. At some cases we performed growth directly from B to D and furnace cooling to room temperatur (TR). In this method we totally can not use Pt or Pt/Rh crucibles with not really clean or have very small leaks.

To remove the mixture of crystals and the remaining fluxes can be done by pouring hot water and mostly need to be assisted by a gentle mechanical work. The crystals were then cleaned in ultrasonic cleaning bath under Acetone. This step should be performed several times until the yellow washing liquid dissapear. The bundled or un dispersed crystals were removed mechanically. A leaching technique as BF method did not work. Pressing into pellet, decreasing growth rate, and seeding give no significant improvement.

Concerning to bismuth (Bi$_2$O$_3$) flux growth we prepared a CuCrO$_2$ phase by means of sintering then pressed and put on a Bi$_2$O$_3$ powder with ratio of 1 : 6. The heating profile could follow Fig. 2 with different ramp, dwell and temperatures. Heating up to 1200 to 1220°C then soaked about 10 to 40 hours followed by cooling down to 1020 - 825°C then to room temperature.

To separate of x-tal, the mixtures were firstly set to remove from Pt (or Pt-Rh) crucibles. In this case, the Pt crucibles were heated upside down at 1000 for 1 - 4 hours. Solid mixture of crystal and remaining fluxes and other liquid can be leached using diluted hot nitric acid with ratio of 1 : 3 to tap water. In some cases of bulky shape we could easily leached just in hours but mostly around 4 - 7 days.

Using the FB method we were facing typical technical problems. The crucibles were severely attacked by Bismuth flux. In order to remove the attached as well as incorporated compound on and in to the crucibles we should carefully perform the thermochemical procedures that may vary to each sample and process. It is also necessary using type and amount of appropriate compound that react to the attached compound (flux) but not to the crucibles it self. Decreasing growth rate/introducing Mn and Mg dopants may give rise to insignificant and to change the shape from flaky to bulky of spinel morphology respectively. The later result may need to further experiments.
III. RESULTS AND DISCUSSIONS

The obtaining raw data of sintered powder were put as an input diagram for refinement analyses using GSAS program. All phases were assumed to be crystallized under R-3m. A typical refinement plot of CCO is shown below.

Figure 4 shows that there is no impurity appears in this phase. All peaks are belong to delafossite CuCrO$_2$ structure. Refinement method using GSAS code (2004) under R-3m space group seems to be fitted well with reliability, weighted reliability, and figure of merit Rp, Rwp, and $\chi^2$ respectively show a good agreement between the observed data and the model (calculation). Using the statistical error we can use the parameter obtained as a tool to infer the crystal structure parameters of sample in Table 1.

The room temperature crystal structure of un-doped CuCrO$_2$ is drawn using parameter extracted from refinement result (Table 1). One unit cell is depicted on left side (a), while extended picture is drawn along b and along c as in b and c respectively.

Typical crystal morphology obtained from FD as well as FB methods are shown in Figure 6.

The selected crystal of undoped CuCrO$_2$ were then char-

<table>
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<th>PARAMETER</th>
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<td>c</td>
<td>17.102795</td>
<td>17.105223</td>
<td>17.094282</td>
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<tr>
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FIG. 7: Magnetization of ZFC mode of CuCrO₂ crystal

FIG. 8: Out of plane Cp - T profile of single crystal CuCr₀.₉₇Mn₀.₀₃O₂ at 1 kHz (solid) and 10 MHz (circle). Inset, the same result at low temperature.

characterized their magnetization at different orientation. The resulted data are plotted together with the undoped polycrystal powder (Fig. 4). It is found that the polycrystal sample is laying as average value of those of other direction as predicted by theory. If we look carefully, we found that in plane of 90 degrees to applied field give the same result. When field applied at 120 degrees, the susceptibility would increase its value as well as showing other magnetic transition around 50 K in addition of Neel Temperature $T_N$ around 25. The same result is also shown by crystal when field applied in-plane. We see no significance electrical capacitance of c-direction. Resulted of capacitance measurement of CCO at 1 kHz is depicted in Figure 8.

It is seen that at 1 kHz CCO-Mn did not show any transition from 10 K to 300 K. At higher frequency, 10 MHz, the crystal show a distinct two respective transitions around 70 K and 80 K. Comparing to Fig. Of M-T

IV. CONCLUSION

We show that both method of FD as well as FB can be use to grow delafossite CuCrO₂ crystals. Magnetisation measurement of polycrystal laying among the value obtained by crystal at various directions. Anisotropic magnetization is clearly shown by crystal measured inplane, 120 degrees or diagonal of hexagonal geometry compare to out of plane perpendicular to applied field.

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