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Flux-growth and characterization of $NaCu_2O_2$ single crystals

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Abstract

For the first time $NaCu_2O_2$ single crystals were prepared by a self-flux technique in Pt crucibles. The as-grown crystals have typical dimensions of $7 \times 3 \times 0.1\,mm^3$. Powder and single crystal XRD measurements confirm the high quality of the prepared crystals. All crystals have the orthorhombic structure: $a = 6.2087(1)$ Å, $b = 2.9343(1)$ Å and $c = 13.0648(3)$ Å. DTA-TG and high-temperature optical microscopy studies show that the $NaCu_2O_2$ compound is stable in the temperature range 25–760°C and melts incongruently at 905 ± 5°C in argon atmosphere. Magnetic susceptibility measurements carried out on the single crystals showed clear evidence of antiferromagnetism at $T_N = 12.25$ K.

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1. Introduction

Low-dimensional spin systems are expected to show a rich phase diagram and novel magnetic properties originating from quantum fluctuations. An interesting example is provided by quasi-1D chains of spin $\frac{1}{2}$ Cu^{+2} ions with competing nearest and next-nearest interactions. In compounds characterised by edge-sharing of the Cu–O chains such as $LiCu_2O_2$ the nature of the magnetic interactions between adjacent Cu^{+2} ions is determined by the angle of the Cu–O–Cu bond in the CuO_4 squares. When this angle goes down to 90°, the nearest neighbours (NN) coupling changes from antiferromagnetic (AFM) to ferromagnetic (FM). At the same time the next nearest neighbours interactions (NNN) are expected to be non-vanishing and of AFM nature. From this point of view the $NaCu_2O_2$ compound, which consists of chains of edge-sharing CuO_4 squares running along the *b*-axis and where the angle of the Cu–O–Cu bond is approximately 94°, should have very interesting magnetic properties.

$NaCu_2O_2$ (NCO) was prepared for the first time with the closed-tube technique [1] over 10 years ago. The initial mixture of Cu_2O and Na_2O_2

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oxides (2:1) was partially melted at 650°C, held for 5 days at this temperature and cooled down to room temperature at a rate of 40°C/h. According to the authors report [1] very fine single crystalline grains were extracted from the inhomogeneous product of reaction, and then used for the X-ray investigation. Recently, a pure powder of NCO has been prepared [2], applying the aside-nitrate route [3]. Nevertheless, the melting behaviour and the crystallization region of NCO compound are not established. To the best of our knowledge no attempts have been made to grow single crystals of this compound, probably due to experimental difficulties when dealing with high-reactivity compounds sensitive to moisture and (sometimes) oxygen, showing high volatility of the respective alkaline component and reactivity to all container materials at high temperatures.

In this paper, we report the first successful growth of NCO single crystals by the self-flux technique. The as-grown crystals were characterized by powder and single crystal X-ray diffraction. The melting behaviour was established using a high-temperature optical microscope (HTOM), quench and DTA-TG measurements. Finally, the magnetic properties of the single crystals were investigated with susceptibility measurements.

2. Experimental procedure

Our preliminary growth experiments were done by using a mixture of NaOH (99.99%) and Na_2O (97%) with 4:1 weight ratio as the flux and CuO (99.9%) as the source material. The mass of the flux was 7.0–8.0 g, and the mass of the copper oxide (II) was 2.4–2.6 g. The mixture was put in a Pt crucible covered with a tight Pt lid, heated up to 600°C and then held 10–12 h at this temperature. Finally, it was cooled down to 300°C at a cooling rate of 2–3°C/h. All experiments were carried out in a pure argon (5N) atmosphere. After growth the residual flux was dissolved in methanol at room temperature in air. However, only small needle-like crystals of NCO with typical dimensions of $0.1 \times 0.5 \times 5\,mm^3$ were obtained by this technique. Large size and plate-like single crystals of NCO could be grown by an improved technique, i.e. the self-flux method. The initial composition was a mixture of Na_2O(97%) and CuO (99.9%) with a 1:5 weight ratio. A total load of 50–60 g, weighed and mixed in a box filled with argon, was put in a Pt crucible covered with a tight Pt lid and heated to 940°C. The soak time was 1–2 h, the crystallization range 940–870°C and the cooling rate 1.5–2.0°C/h. The residual flux was decanted at 860–870°C in order to get free-standing NCO single crystals. The growth experiments were performed in an argon flow (5N).

The thermal stability of the NCO compound was investigated by DTA-TG. Small needle-like crystals of NCO were heated in the DTA-TG apparatus (NETZSCH STA-449C) at 10 K/min up to 1000°C in Ar (5N) flow. A Pt crucible without lid was used. A high temperature optical microscope "Olympus" MS-11 equipped with an optical heating system (MS-E1S/VMC-1 from "ULVAC-RICO", Japan) was employed to visualise the melting point of the single crystals of NCO. Small MgO and Pt crucibles with a diameter of 4 mm were used. Prior to the measurement, the temperature control system was calibrated by measuring the melting points of Au(5N), Ag(5N) pure metals.

A compositional analysis of materials was carried out by induction-coupled plasma atomic emission spectroscopy (ICP-AES) and powder X-ray diffraction (XRD, "PHILIPS" PW-3710). X-ray diffractogram of a powder sample in a capillary holder was taken at a room temperature on a STOE STADI P diffractometer with MoK_α-radiation ($\lambda = 0.7093$ Å). The powder sample was prepared by grinding of the single crystal. A position sensitive detector and a curved germanium monochromator were used to collect data in the angular range $10° < 2\theta < 90°$.

The magnetisation of a single crystal of $NaCu_2O_2$ was measured as a function of temperature in a superconducting quantum interference device magnetometer ("Quantum Design", model MPMS 7.0). Prior to the measurement, the sample was cooled down to 2 K in zero magnetic field. A magnetic field of 0.1 T was then applied parallel to the *b*-axis of the crystal and the magnetisation was measured on warming up to 325 K.

3. Results and discussion

3.1. Growth and crystal perfection

Fig. 1 shows typical plate-like NCO crystals with dimensions of $7 \times 3 \times 0.1\,mm^3$ grown by a self-flux method. All crystals are black with a metallic lustre and have the (a,b) habit. ICP-AES analysis shows that all grown crystals have the correct stoichiometry Na:Cu = 1:2, and no Pt was detected. It should be mentioned that among all crucible materials (Pt, Pt/Au, Au, Ag, YSZ, Al_2O_3) only pure platinum crucibles were stable against the melt corrosion in argon flow.

Fig. 2 shows a powder XRD pattern of the as-grown NCO crystal. All reflections can be indexed in the orthorhombic space group Pnma. No traces of impurity phases were found in the sample. The spurious peak (marked as C) between the (0 0 6) and (2 0 1) Bragg-reflections arises from the experimental set-up (i.e. from the collimator). The lattice parameters derived from the powder XRD data are: $a = 6.2087(1)$ Å, $b = 2.9343(1)$ Å and $c = 13.0648(3)$ Å. Fig. 3(a) illustrates single-crystal XRD pattern taken on the c-face of the as-grown crystal of NCO. Only sharp {0 0 l} peaks can be observed, indicating the high crystalline quality of the sample. The c-axis parameter derived from the XRD pattern is 13.07(2) Å. The X-ray rocking curve measured on a single crystal of NCO is given in Fig. 3(b). The profile of the

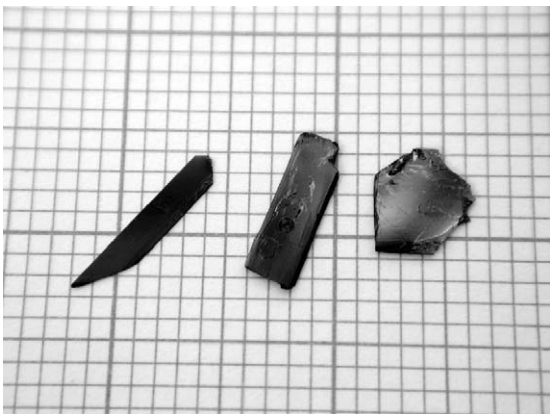

Fig. 1. As-grown NCO single crystals, the small grid division is 1 mm.

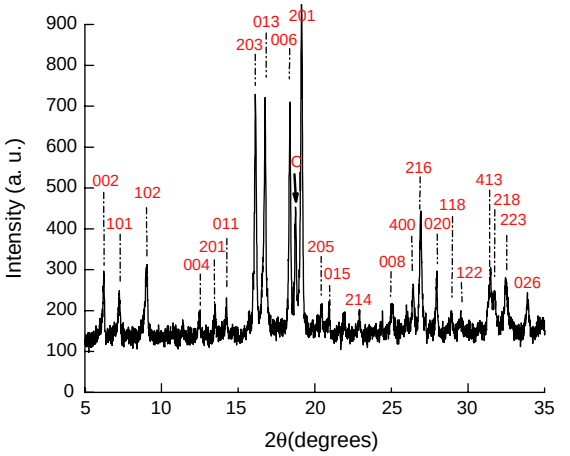

Fig. 2. Powder XRD pattern of the as-grown NCO crystal. All peaks corresponded to the pure $NaCu_2O_2$ phase (MoK_α-radiation).

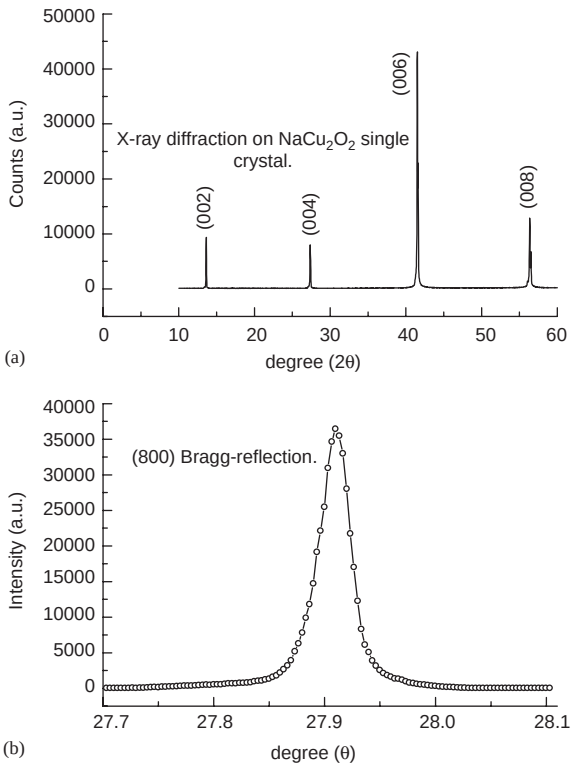

Fig. 3. (a) Single-crystal XRD pattern for the c-face of the as-grown NCO crystal (CuK_α-radiation) and (b) X-ray rocking curve of $NaCu_2O_2$ crystal, (8 0 0)—Bragg-reflection, (MoK_α-radiation).

(8 0 0) Bragg-reflections has a FWHM of 0.03° at room temperature, indicating the excellent crystal quality of the sample.

3.2. Crystallization temperature and melting behaviour

The melting point of NCO measured by HTOM was found to be 905 ± 5°C in argon (5N) atmosphere. After melting the liquid phase was slowly cooled down. It was completely solidified below 843 ± 5°C. Therefore, the crystallization region of the NCO phase is between 843°C and 905°C in argon atmosphere. It was nearly the same in an $Ar/O_2 = 100/0.3$ mixture. The melting point at 905 ± 5°C, found by HTOM, correlates well with the beginning of the peak on the DTA curve for a single crystal of the NCO compound (Fig. 4a).

The flux, decanted at 860–870°C, was solidified in a Pt crucible on cooling to room temperature. Powder XRD measurements showed that it consists of only two phases: $NaCu_2O_2$ and NaCuO (the last one is not stable in air). Based on these data, we assume the existence of an eutectic between $NaCu_2O_2$ and NaCuO compounds at 843 ± 5°C in argon atmosphere.

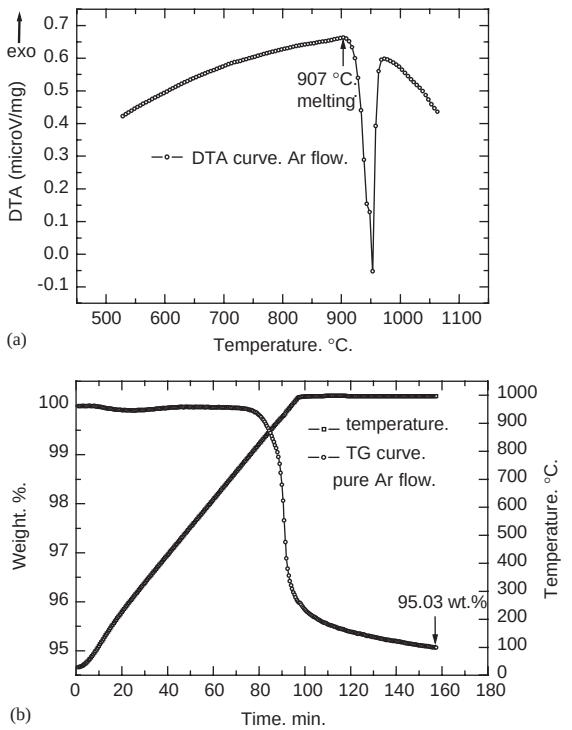

Fig. 4. DTA curve (a) and TG curve (b) of NCO crystal in argon flow.

The melting behaviour of the NCO phase was further studied by the frozen drop technique in argon (5N) flow. The method is well described in Ref. [4]. At first, the molten drop was formed by fusion of a feed rod of $NaCu_2O_2$ in a four mirror-type furnace (CSI, Japan). The molten drop was then allowed to homogenize for 10 min. Finally, the drop was frozen within 2 s by turning off the lamp power. The composition of the quenched drop was analyzed by powder X-ray diffraction. Only Na_2CO_3 and Cu_2O/CuO phases were detected. CuO was formed by partial oxidation of Cu_2O during the cooling, and Na_2CO_3 is the product of the reaction between Na_2O and CO_2 in air during the grinding. Thus, initially the frozen (molten) drop consists of Na_2O and Cu_2O oxides. It means that the composition of the molten drop differs from the composition of the feed rod of $NaCu_2O_2$. We conclude that the $NaCu_2O_2$ phase melts incongruently at 905 ± 5°C in argon atmosphere.

The thermal stability of $NaCu_2O_2$ was studied by the TG technique in argon (5N) flow. Weight changes in the sample are shown in Fig. 4b as a function of temperature. No weight changes were detected in the temperature range 25–760°C. A weight change of 4.97 wt% was measured at 1000°C. The decomposition of CuO to CuO_x ($x \approx 0.5$) in a liquid phase at these temperature and partial oxygen pressure [5] leads to a weight loss of 4.4 wt%. This means that the weight loss due to the Na_2O evaporation is about 0.6 wt% per hour at 1000°C. The weight fraction of the Na_2O is about 17 wt% in the initial mixture. Thus, the growth time did not exceed 2 days in our experiments in order to avoid the evaporation loss of the Na_2O. The best crystals (Fig. 1) were obtained when 1 wt% of Na_2O was added to initial mixture to compensate the evaporation effect. But another phase, NaCuO, was mainly crystallized when over 5 wt% of Na_2O was added. Thus, the crystallization region of $NaCu_2O_2$ compound lies between 78.7 and 83.7 wt% of CuO (in initial mixture).

All attempts to prepare NCO crystals by top seeded solution growth and floating zone techniques were lack due to the strong evaporation of Na_2O from a melt surface.

3.3. Magnetic and resistivity measurements

The zero field cooled susceptibility shows a magnetic transition to a Neel ordered state at $T_N = 12.25\,K$ (Fig. 5). The high temperature susceptibility ($150\,K < T < 300\,K$) follows a Curie–Weiss law (Fig. 5, inset) with a negative Curie temperature $\vartheta = -21.73\,K$, indicating that the nature of the magnetic interactions is predominantly antiferromagnetic. The effective magnetic moment, μ_{eff}, calculated per 1 mol of $NaCu_2O_2$ is $1.8\mu_B$. It corresponds to one unpaired electron per mol of $NaCu_2O_2$ (theoretical value $1.73\mu_B$). The calculated value, $\mu_{eff} = 1.8\mu_B$, correlates well with the assumption of the mixed valence state of copper atoms in the structure: half of copper atoms are in the valence state Cu^{+1} ($s = 0$) and the other half is in the valence state Cu^{+2} ($s = \frac{1}{2}$). The neutron diffraction experiments have been performed on powder samples to solve the magnetic structure and it has been found that the frustration leads to an incommensurability of the spin arrangement [6].

Preliminary resistivity measurements (4-points technique) show an insulating behaviour for the conductivity of the single crystals of NCO.

4. Conclusions

It was established that the $NaCu_2O_2$ compound melts incongruently at $905 \pm 5^{\circ}C$ in argon atmosphere and single crystals could be obtained by the self-flux technique. The as-grown crystals are as large as $7 \times 3 \times 0.1\,mm^3$. The high quality of the

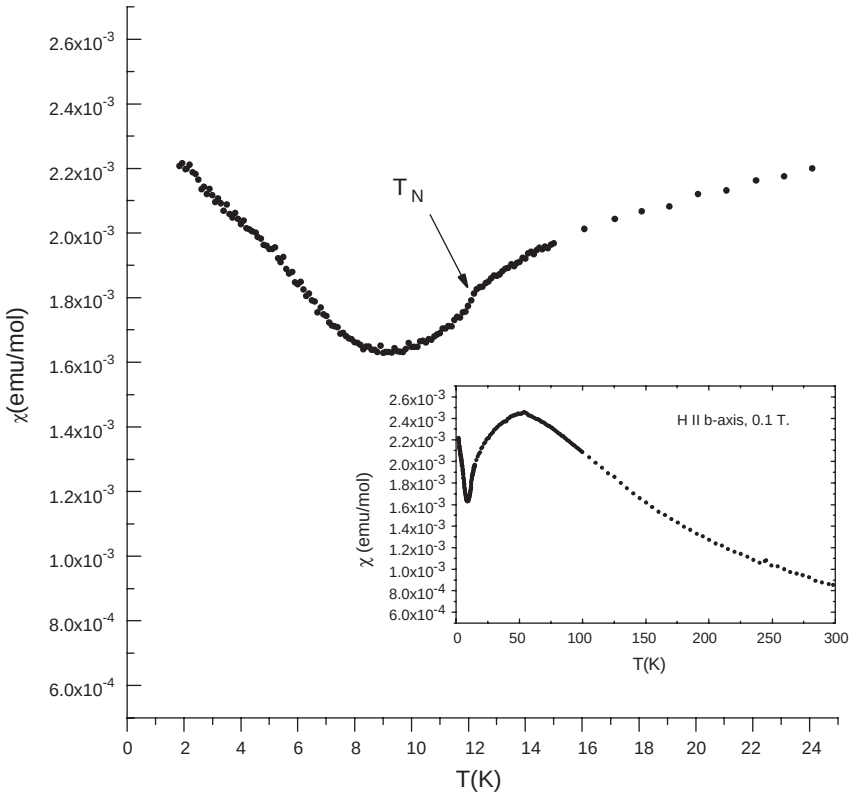

Fig. 5. Magnetic susceptibility as a function of temperature for the $NaCu_2O_2$ single crystal.

prepared crystals was assessed by powder and single crystal XRD measurements. $NaCu_2O_2$ single crystals showed clear evidence of antiferromagnetism.

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