

## Crystal Growth and Structure Refinement of NaCuO<sub>2</sub> by X-Ray and Neutron Diffraction

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Single crystals of sodium oxocuprate(III) NaCuO<sub>2</sub> with up to 5 mm length have been prepared from sodium hydroxide/peroxide melts. The structure has been refined by single crystal X-ray and neutron powder data. The Laue symmetry has been determined now unambiguously to be *2/m*, resulting in a monoclinic Bravais lattice. © 1990 Academic Press, Inc.

### Introduction

The importance of highly oxidized states, i.e., Cu(III) and anion *p* band holes for superconductivity in polynary oxocuprates, has been discussed recently (1, 2). For reliable spectroscopic studies reference compounds containing Cu(III) are required. The first simple oxocuprate(III) compounds ACuO<sub>2</sub> (*A* = alkali) have been described by Klemm and Hoppe (3-6). Single crystal X-ray structure investigations could be performed for KCuO<sub>2</sub> (5) whereas a structure model for NaCuO<sub>2</sub> has been based on powder X-ray data (6). Recently a neutron diffraction study on NaCuO<sub>2</sub> has been reported (7) which concludes that this compound is not triclinic as described originally but monoclinic with the space group *C2/m*. Since the present discrepancy can only be re-

solved unambiguously by single crystal structure studies we have decided to investigate crystal growth conditions for NaCuO<sub>2</sub>. A further reason for the attempt to prepare larger single crystals originates from the fact that the alkali oxocuprates are reported to be extremely sensitive to ambient air. Since photoelectron spectroscopy has a rather low information depth, even minor surface contamination can lead to erroneous results. Investigations on larger single crystals which are crushed *in situ* under high vacuum conditions could therefore yield more reliable data on the bulk properties.

We present here our results on crystal growth studies and on single crystal X-ray well as neutron powder studies of sodium oxocuprate(III).

### Preparation and Properties of NaCuO<sub>2</sub>

Earlier studies on the preparation of the sodium oxocuprate(III) in polycrystalline form were performed by solid state reactions between copper-II-oxide and sodium

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peroxide under an atmosphere of dry oxygen (4–6). The products obtained were described as polycrystalline material with high sensitivity to air and water. We observed that single crystals of NaCuO<sub>2</sub> can be easily obtained by reaction of commercial CuO powder in an excess of either sodium hydroxide or sodium hydroxide/sodium peroxide melt at temperatures between 400 and 600°C in ambient atmosphere with reaction times between 1 and 4 days. Detailed investigations demonstrated that the reaction is in principle dependent upon the partial pressures of water and oxygen; the following descriptions pertain only to reactions under an atmosphere of normal air.

The reaction of CuO in NaOH melt yields single crystal needles up to 5 mm in length at 450°C within 24 hr; the yield remains very low, however (ca. 2%) and does not increase significantly upon increasing the reaction time. Quantitative conversion of CuO to NaCuO<sub>2</sub> is achieved by using a mixture of NaOH/Na<sub>2</sub>O<sub>2</sub>. We give here a description of a reproducible procedure: 50 g of NaOH, 18 g of Na<sub>2</sub>O<sub>2</sub> and 2.2 g of CuO are mixed and transferred into a flat platinum vessel (diameter ca. 80 mm). The vessel is heated up in a furnace within 2 hr to 450°C, kept at this temperature for 3 days, cooled down to 300°C within 1 h, removed from the furnace, and placed into an exsiccator until room temperature is reached. The solidified melt is rapidly washed with alkaline ice water; adherent water is removed subsequently by washing with acetone and drying under high vacuum at ambient temperature.

The reaction product (yield 98%) consists uniformly of needles of a brilliant blue color and metallic luster and an average length of 1 mm. In transparent light the edges of the crystals appear red; preliminary two-point measurements indicate a high resistivity.

We observed that large crystals with a length of 3–5 mm can be obtained quantitatively via liquid phase transport if the reaction described above is carried out at 600°C

with a small furnace temperature gradient (ca. 20–40°C) across the vessel. CuO is placed into the hot zone; the small crystals formed are transported within 20 hr to the colder zone. The vessel is kept after this process for 1–2 days at 450°C and the crystals are recovered from the melt as outlined above.

On extended exposure to air, the surface of the crystals slowly darkens; in water slow hydrolysis is observed. The final product of the decomposition process is black-brown polycrystalline CuO showing strong broadening of X-ray lines.

With aqueous mineral acids stable toward oxidation instantaneous decomposition with complete dissolution is observed under formation of dioxygen. The thermogravimetric studies in O<sub>2</sub> atmosphere showed two successive transitions starting at 400 and 600°C, respectively. Electrogravimetric determination of the Cu content yielded the value calculated for NaCuO<sub>2</sub> (99%).

Experiments in alumina, silver, gold, and nickel vessels yielded identical products; analytical data confirmed that only traces of the container materials are present in the crystals. The relatively high stability toward air and water—allowing easy recovering of the crystals from the melt—is obviously a kinetic effect originating from low defect concentration and absence of grain interfaces present in polycrystalline material.

X-ray powder Guinier data (300 K, CuK $\alpha$ ) of ground single crystals yielded the following lattice parameters on the basis of the triclinic unit cell (pm) described in (6):

$$\begin{aligned} a &= 274.2(3), & \alpha &= 76.30(7)^\circ \\ b &= 665.4(7), & \beta &= 113.35(5)^\circ \quad (Z = 1) \\ c &= 345.6(3), & \gamma &= 128.05(7)^\circ \end{aligned}$$

#### Structure Refinement of NaCuO<sub>2</sub> by Single Crystal X-ray Data

The powder X-ray data of NaCuO<sub>2</sub> obtained by Hestermann and Hoppe (6) led the

authors to the assumption of a triclinic unit cell with the space group  $P\bar{1}$ . Brese *et al.* (7) found that this unit cell can be transformed into a doubled cell with the higher monoclinic symmetry and space group  $C2/m$ . They performed a new structure determination by neutron diffraction data of polycrystalline material using Rietveld profile refinement. We were now able to carry out for the first time a single-crystal X-ray study on  $\text{NaCuO}_2$  at 300 K. Our investigations confirm basically the results obtained by Brese *et al.* (7).

The compound has a monoclinic unit cell with the space group  $C2/m$  (International Tables No. 12). An oscillation photograph around the monoclinic  $b$  axis displayed mirror symmetry; a comparison of the intensities of symmetry equivalent reflections indicated the Laue group  $2/m$ . From the systematic extinctions of reflections  $kh$  with  $h + k = 2n + 1$  results a C-centered Bravais lattice; the successful refinement confirms the centrosymmetric space group  $C2/m$ .

The determination of the lattice parameters and the measurement of the intensities were carried out on a four-circle diffractometer Syntex  $P2_1$  using  $\text{MoK}\alpha$  radiation with graphite monochromator. Monoclinic lattice parameters were extracted by least squares refinement of 15 reflections with  $2\theta \leq 25^\circ$ :  $a = 636.3(2)$  pm,  $b = 275.3(1)$  pm,  $c = 611.0(1)$  pm, and  $\beta = 120.78(2)^\circ$ .

The intensities of 1134 reflections with  $2\theta \leq 80^\circ$  and  $-11 \leq h \leq 11$ ,  $-4 \leq k \leq 4$ ,  $-10 \leq l \leq 10$  (full sphere) were measured in the  $\omega$ -scan technique; the measuring velocity (dependent upon the reflection intensity) was  $1.50\text{--}29.30^\circ \text{ min}^{-1}$ . Intensities of two control reflections were redetermined after ca. 200 measurements; they exhibited only statistical variations. Intensities of symmetry equivalent reflections were averaged after numerical absorption correction (crystal size  $0.045 \times 0.05 \times 0.12 \text{ mm}^3$ ,  $\mu = 113.6 \text{ cm}^{-1}$ , Lorentz and polarization correction,

$R = 0.027$ ); 326 symmetry-independent reflections resulted.

We found that the monoclinic cell can also be transformed to a (pseudo-)orthorhombic F-centered cell with lattice constants  $a = 636.3$  pm,  $b = 1049.9$  pm, and  $c = 275.3$  pm, using a transformation matrix

$$\begin{Bmatrix} -1 & 0 & 0 \\ 1 & 0 & 2 \\ 0 & 1 & 0 \end{Bmatrix} \begin{Bmatrix} a_m \\ b_m \\ c_m \end{Bmatrix} = \begin{Bmatrix} a_o \\ b_o \\ c_o \end{Bmatrix}.$$

However, the internal consistency index  $R$  for merging equivalent reflections assuming Laue group  $mmm$  is unreasonably high (0.261 vs 0.027 for monoclinic symmetry,  $2/m$ ). Therefore we conclude, that the choice of the monoclinic space group is correct.

For the structure refinement the model proposed by Brese *et al.* (7) was used. The calculations were carried out with the program SHELX 76 and atomic scattering factors from Cromer and Mann (8) for  $\text{Cu}^{2+}$  and  $\text{Na}^+$  and from Hovestreydt for  $0^{2-}$  (9). Exact scattering factors for  $\text{Cu}^{3+}$  were not available; calculations after Moore (10) with analytical constants for the extrapolation of the scattering factor of  $\text{Cu}^{3+}$  did not lead to satisfying results.

The anisotropic refinement was converging at a  $R$  value of 0.0297 and  $R_w = 0.0278$ , respectively ( $w = 1/[\sigma^2(F) + 0.004F^2]$ ). A final difference Fourier synthesis displayed only minor residual electron densities ( $<1 \times 10^{-6} \text{ e pm}^{-3}$  close to the positions of the Cu ions. Atomic parameters and isotropic temperature factors are given in Table I, bond length and bond angles in Table II.

### Neutron Powder Diffraction Data

The material used was a sample of 5 g of crystals prepared as described above with approximately statistical orientation and a small residual CuO content in a vanadium container. The data were collected at 300 K

TABLE I  
ATOM PARAMETERS OF NaCuO<sub>2</sub>

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>13</sub>
Cu	0	0	0	0.0083(2)	0.0036(2)	0.0077(2)	0.0027(1)
Na	0	1/2	1/2	0.0122(5)	0.0103(6)	0.0139(6)	0.0052(5)
O	0.3330(3)	0	0.7762(3)	0.0122(5)	0.0052(6)	0.0095(5)	0.0025(4)

TABLE II  
BOND LENGTHS AND BOND ANGLES (°) IN NaCuO<sub>2</sub>

Atoms	Bond lengths	Atoms	Bond angles
Cu-O(4)	184.6(1)	O-Cu-O(2)	180.00
Na-O(4)	236.1(1)	O-Cu-O(2)	96.44(5)
Na-O(2)	241.1(1)	O-Cu-O(2)	83.56(5)

and at 4.2 K at the D2B and D1A instruments of the high flux reactor of the ILL in Grenoble. The structure refinement was performed with Rietveld profile analysis using the STRAP program system(11, 12). At 300 K the measured angular range corresponded to 15–160° (2θ) with λ = 159.5 pm, at 4.2 K to 15–150° (2θ) and λ = 190.9 pm.

The refinement of the data was performed with the space group C2/m after Brese *et al.* (7). Table III represents a list of the structural parameters obtained by the calculation of 119 reflex profiles. Seventeen parameters were used in the refinement, among these the scale factor, six positional parameters, the occupation factor of oxygen, individual isotropic temperature factors, three reflec-

tion profile parameters (pseudo-Voigt function), one parameter for compensation of a partial preferred orientation of the NaCuO<sub>2</sub> needles along 010, and a further parameter for correction of asymmetric reflection profile curves. For the adaptation of the small amount of CuO contamination a separate scale factor was used. Figure 1 shows the Rietveld profile refinement for NaCuO<sub>2</sub> at 300 K.

The monoclinic unit cell can be transformed back to the triclinic cell reported by Hestermann *et al.* (6) with the following matrix

$$\begin{pmatrix} 0 & -1 & 0 \\ 1/2 & 3/2 & 1 \\ -1/2 & 1/2 & 0 \end{pmatrix} \begin{pmatrix} a_m \\ b_m \\ c_m \end{pmatrix} = \begin{pmatrix} a_{tr} \\ b_{tr} \\ c_{tr} \end{pmatrix}.$$

The relationship between the two unit cells is indicated in Fig. 2; the vectors for both systems were selected on the basis of a clockwise rotation.

The refined positional factor for the oxygen atoms converged at  $n = 0.95$ , corresponding formally to NaCuO<sub>1.90</sub>. It is most likely that this effect is due to a texture ef-

TABLE III  
STRUCTURE PARAMETERS FOR NaCuO<sub>2</sub> AT 300 K IN C2/m NEUTRON POWDER DIFFRACTION DATA

Atom	x	y	z	U <sub>iso</sub> (Å <sup>2</sup> ) × 10 <sup>-2</sup>	n
Na	0	1/2	1/2	2.23(11)	0.05
Cu	0	0	0	1.27(8)	0.05
O	0.3334(2)	0	0.7767(3)	0.99(7)	0.93(2)

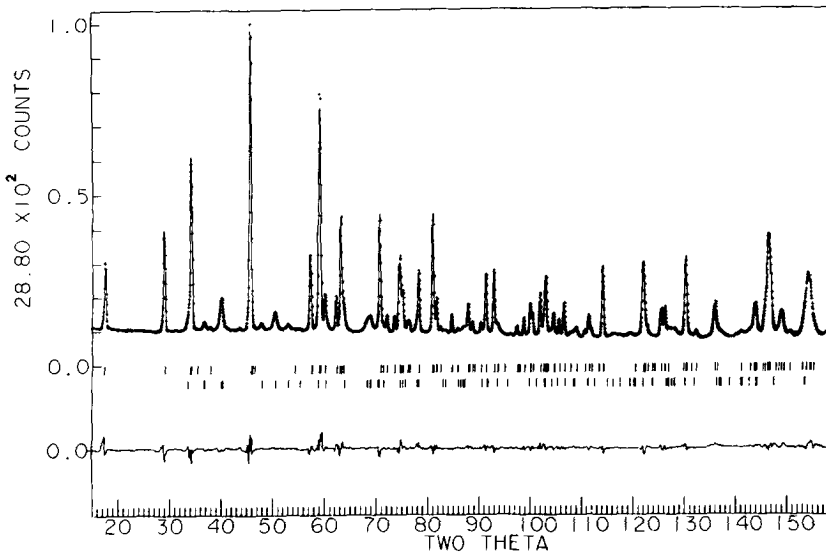


FIG. 1. Rietveld profile refinement for  $\text{NaCuO}_2$ . The calculated curve is represented by a solid line, data points are shown as crosses. Indicated are the difference plots at the bottom and the peak positions (upper marks for  $\text{NaCuO}_2$  and lower for  $\text{CuO}$  reflections).

fect, i.e., partial orientation of the needle-shaped crystals, which could not be compensated completely by the preferred orientation parameter.

In order to detect potential distortions or phase transitions of  $\text{NaCuO}_2$  at low temperatures the sample was measured in addition at 4.2 K. Since no further reflections or intensity changes could be observed, it was concluded that no structural changes appeared down to 4.2 K. The refinement was carried out again with the space group

$C2/m$ ; lattice parameters are  $a = 635.81(1)$ ,  $b = 275.04(1)$  and  $c = 610.88(2)$  pm with  $\beta = 120.752(1)^\circ$  for 300 K and  $a = 630.15(1)$ ,  $b = 2.7437(1)$  and  $c = 605.87(1)$  pm with  $\beta = 120.473(1)^\circ$  for 4.2 K. The small changes observed in the lattice parameters upon cooling concern essentially only the  $a$  and  $c$  axes; obviously a corresponding decrease of the  $b$  axis is avoided since  $\text{Na}^+/\text{Na}^+$  distances are already rather short.

## Discussion

The structure scheme of  $\text{NaCuO}_2$  is given in Fig. 3. Chains of edge sharing planar  $\text{CuO}_4$  units traverse the crystal in the direction of the monoclinic  $b$  axis. The Cu ions occupy special positions ( $2a$ ) on symmetry centers. Similarly the  $\text{Na}^+$  ions are on special positions ( $2d$ ) on symmetry centers; they are coordinated by oxygen anions (positions  $4i$ ) with a distorted octahedral environment and connect neighboring chain units. The coordination of  $\text{Na}^+$  is indicated in Fig. 3.

The Cu–O bond length in  $\text{NaCuO}_2$  with 184.3 pm is practically identical with that of

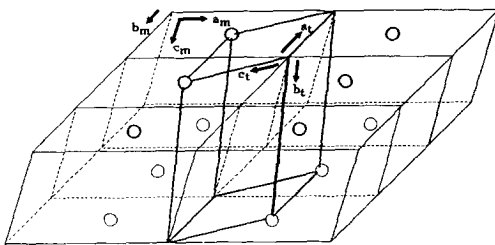


FIG. 2. Arrangement of the triclinic unit cell on the base of the monoclinic lattice. For an easy survey only the C-centered Cu atoms are outlined (for transformation matrix c.f. text).

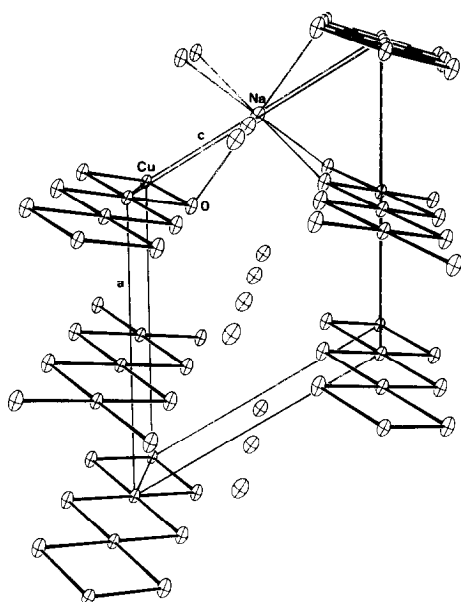


FIG. 3. Structure scheme of NaCuO<sub>2</sub>. The coordination of Na and Cu by oxygen and the unit cell is outlined.

KCuO<sub>2</sub> (183 pm) (7). However, while in KCuO<sub>2</sub> the CuO<sub>4</sub> units of neighboring CuO<sub>4/2</sub> chains are stacked parallel to each other, a translation of the chains relative to each other is observed for NaCuO<sub>2</sub>, leading to distorted trigonal prismatic sites between the copper oxygen chains. This translation in turn leads to a P2 stacking mode (c.f., below) and the existence of Na/O octahedral planes, which is obviously a consequence of the lower ionic radius of Na<sup>+</sup> as compared to that of K<sup>+</sup>, which prefers the trigonal prismatic K/O environment in KCuO<sub>2</sub>. The NaO<sub>6</sub> octahedra share edges in the *a/b* plane; along 102 the octahedral planes are connected via face sharing distorted trigonal prisms.

For the oxygen atoms a stacking sequence ABBA of the P2 type (Fig. 4) therefore results similar to the stacking mode found in certain lamellar alkali transition metal oxides AMO<sub>2</sub> (13). A description of NaCuO<sub>2</sub> on the basis of a stacking mode ABC such

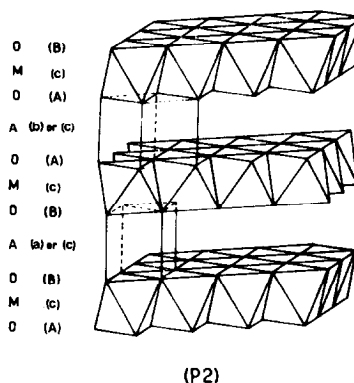


FIG. 4. P2 stacking scheme for ternary oxides AMO<sub>2</sub> (A = alkali, M = transition metal) (13). In NaCuO<sub>2</sub> the centers of the trigonal prisms are empty, while the transition metal atoms are located at the face centers of the distorted prisms.

as in  $\alpha$ -NaFeO<sub>2</sub>, which has been given in Ref. (7) seems not to be appropriate.

The formation of a high valent oxocuprate and the corresponding single crystals from alkali hydroxide/peroxide melts under isothermal condition or via flux transport at low temperatures seems to be an interesting technique for further studies on related oxometallate phases with transition metals in high oxidation states.

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