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# Synthesis and characterization of $Na_{11}[CuO_4][SO_4]_3$

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## Abstract

$Na_{11}[CuO_4][SO_4]_3$ was obtained from a redox reaction of CuO with $Na_2O_2$ in the presence of $Na_2O$ and $Na_2SO_4$ in sealed Ag containers under Ar atmosphere at 600°C. The crystal structure has been determined from X-ray single crystal data at 293 and 170 K (*Pnma*, $Z = 4$). The lattice parameters have been refined from X-ray powder data at 293 K as well: $a = 1597.06(6)$ pm, $b = 703.26(3)$ pm, $c = 1481.95(6)$ pm. The structure contains isolated distorted square-planar $[CuO_4]^{5-}$ anions and non-coordinating sulfate groups. Furthermore, we report calculations of the Madelung Part of the Lattice Energy (MAPLE) and some of the physical properties of $Na_{11}[CuO_4][SO_4]_3$.

*Keywords:* Crystal structure; Copper; Sodium; Sulfate

## 1. Introduction

Alkaline metal oxocuprates(III), $ACuO_2$ with $A =$ Li–Cs, have been studied and structurally characterized by Hoppe et al. [1]. These oxocuprates(III) contain square-planar $[CuO_4]$-units connected via edges to chains. The structural feature of dimeric complexes $[O_2CuO_2CuO_2]^{6-}$ is found in $Li_3CuO_3$ and $Na_3CuO_3$ [2]. Isolated anions $[CuO_4]^{5-}$ are observed for $Ba_4Li[CuO_4][CO_3]_2$ and $Ba_4Na[CuO_4][CO_3]_2$ [3]. The latter compounds are quite unique in respect to non-coordinating carbonate groups. Recently, some more examples have been found containing isolated oxometallates and non-coordinating anions like $Na_5[MO_2][X]$ with $M = Co^+, Ni^+, Cu^+$ and $X = S^{2-}, SO_4^{2-}, CO_3^{2-}$ [4] or $Na_8[CoO_3][SO_4]_2$ [5]. These compounds contain the transition metal in an unusual coordination sphere, e.g. C.N. 2 (linear) and 3 (trigonal-planar), respectively. Our aim was to find out, if this sequence can be extended to C.N. 4 with a square-planar coordination of the transition metal, e.g. Cu(III) with $3d^8$ configuration.

To our knowledge no single crystal data has been reported for an alkaline metal oxocuprate(III) sulfate so far. Whereas for copper in the divalent oxidation state a structure determination of $KNaCu_3O(SO_4)_3$ (mineral name: Euchlorine) has been reported with a square-pyramidal coordination of copper consisting of three sulfate groups and one oxide [6].

Stabilization of the trivalent oxidation state for copper can be achieved in coordination chemistry under oxidizing conditions and examples are $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ [7] and $Na_5[Cu\{TeO_4(OH)_2\}_2] \cdot 16H_2O$ [8]. In these cases the $[Cu^{III}O_4]$-unit is stabilized by two chelating oxocomplexes, e.g. $[IO_6]^{5-}$ and $[TeO_4(OH)_2]^{4-}$, respectively.

Here we report the synthesis, crystal structure and some physical properties of $Na_{11}[CuO_4][SO_4]_3$ [9].

## 2. Experimental details

Transparent ruby-red single crystals of $Na_{11}[CuO_4][SO_4]_3$ were obtained from a redox reaction of CuO with $Na_2O_2$ in the presence of $Na_2O$ and $Na_2SO_4$ (molar ratio: 2:1:4:6) in sealed Ag containers under inert gas atmosphere (Ar) at 600°C (21*d*). For protection reasons the containers were encapsulated in silica

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ampoules. The product is very sensitive to moisture and decomposes in ambient atmosphere. Therefore, all preparations and selection of single crystals were carried out in a glove-box (M. Braun). X-ray diffraction data of single crystals, which have been sealed under Ar atmosphere in glass capillaries, were collected on an IPDS diffractometer (Stoe&Cie). The program system X-RED and X-SHAPE [10] was used for numerical absorption correction and SHELX-S and SHELX-L [11] for structure determination. X-ray powder diffraction data were collected on a STADI-P diffractometer (Stoe&Cie) using the capillary technique and monochromatic (Ge) Cu-$K\alpha$ radiation. Infrared spectra of $Na_{11}[CuO_4][SO_4]_3$ (ground crystals pressed in KBr pellets) were recorded on a Bruker spectrometer (IFS-66v/s) under vacuum and UV-VIS spectra on a CARY E05 (Varian) spectrometer under Ar-atmosphere. EPR measurements were carried out on a Bruker X-band spectrometer (9.47 GHz) in the temperature range from 2 to 300 K.

## 3. Results and discussion

### 3.1. *Crystal structure of* $Na_{11}[CuO_4][SO_4]_3$

For crystallographic data and details of the structure determination see Tables 1 and 2. Systematic absences of reflections indicated the space group *Pnma* or $Pn2_1a$. Refinement in the non-centrosymmetric space group resulted in no significant change in the *R*-factors, but gave rise to numerous correlations between symmetry related atoms. Furthermore, the statistical orientation of one sulfate group occurred as well, see below. Therefore, the structure was finally solved in the centrosymmetric space group, *Pnma*.

The characteristic structural features are isolated distorted square-planar $[CuO_4]^{5-}$ anions and non-coordinating sulfate groups, Fig. 1. For one of the three crystallographically independent $[SO_4]^{2-}$ anions two principal statistical orientations occur. Therefore, we collected a single-crystal X-ray data set at 170 K to check for a possible ordering as well and found the same split positions for the oxygen atoms O32, O33, O34 and O35 belonging to $[S3O_4]^{2-}$. In Figs. 2(A) and (B) Difference-Fourier maps of the (001) plane at $z = 0$ are shown at 293 and 170 K without the refinement of the O32, O33, O34 and O35 atomic positions. Electron density is observed in approximately $\bar{d} = 148$ pm distance around S3 with four positions of main density. This illustrates the statistical orientation of the $[S3O_4]^{2-}$ anion in the plane perpendicular to the *z*-axis with the S3–O31 interatomic distance in the [001] direction. Refinement of the O32, O33, O34 and O35 atomic positions and site occupation factors with coupled anisotropic and isotropic displacement factors for O32, O33 and O34, O35, respectively, gives a principal picture of the situation and is illustrated in Figs. 2(C) and (D). Since X-ray diffraction data present only an average picture of the scenario a rather poor agreement of the derived interatomic distances and angles for the $[S3O_4]^{2-}$ anion with the expected $T_d$ symmetry of a sulfate group is observed. The other two sulfate groups $[S1O_4]^{2-}$ and $[S2O_4]^{2-}$ are of almost ideal tetrahedral symmetry with typical interatomic distances for this anion, see Table 3.

Table 1
Crystallographic data for $Na_{11}[CuO_4][SO_4]_3$

| | | |
|---|---|---|
| Crystal system | Orthorhombic | |
| Space group | *Pnma* | |
| Temperature (K) | 293 | 170 |
| Lattice constants (pm) | $a = 1601.6(2)$<br>$b = 705.78(7)$<br>$c = 1490.2(2)$ | 1600.5(3)<br>701.72(8)<br>1480.1(2) |
| Formula per unit cell | $Z = 4$ | |
| Diffractometer | Stoe IPDS | |
| Radiation (Mo$K\alpha$) | 71.073 pm | |
| Monochromator | Graphite | |
| Range ($2\Theta_{max}$) | 56.26°<br>$-19 \leqslant h \leqslant 18$<br>$-9 \leqslant k \leqslant 8$<br>$-19 \leqslant l \leqslant 19$ | 56.20°<br>$-21 \leqslant h \leqslant 21$<br>$-8 \leqslant l \leqslant 8$<br>$-19 \leqslant k \leqslant 18$ |
| *F*(000) | 1304 | |
| Absorption correction | Numerical (10) | |
| Absorption coefficient ($mm^{-1}$) | $\mu = 2.04$ | $\mu = 2.06$ |
| No. of measured reflections | 14928 | 14665 |
| No. of unique reflections | 1917 | 1946 |
| $R_{int}$ | 0.0823 | 0.0937 |
| Refined parameters | 170 | 170 |
| Goodness-of-fit | 0.996 | 1.017 |
| $R_1[I_0 > 2\sigma(I)]$ | 0.0462 | 0.0496 |
| $R_1$ (all data) | 0.0892 | 0.0924 |
| w$R_2$ (all data) | 0.0979 | 0.1034 |
| Residual electron density (e/Å$^3$) max/min | 1.040/−0.654 | 1.300/−1.136 |
| CSD[a] | 413673 | 413672 |

[a] Further information can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Fax: (+49)7247-808-666, e-mail: crysdata@fiz-karlsruhe.de) by citing the CSD-No.

The interatomic distances, $\bar{d}$(CuO) = 186.6 pm, are in good agreement with data reported in the literature for copper(III), e.g. 185 pm for $Ba_4Na[CuO_4][CO_3]_2$ [3] and $ACuO_2$ [1], although they are slightly longer probably due to small distortions of the complex or a 1–2% impurity of $Cu^{2+}$ on the copper sites, see below.

Seven crystallographically independent sodium cations complete the structure of $Na_{11}[CuO_4][SO_3]_3$. The coordination spheres of these sodium cations are highly distorted square-pyramidal and octahedral polyhedra, respectively, and depend on the orientation of $[S3O_4]^{2-}$. If for example the oxygen positions O32 (2 ×) and O34 are occupied the resulting coordination numbers of the

Table 2
Atomic parameters and equivalent displacement factors (in pm$^2$) for $Na_{11}[CuO_4][SO_4]_3$ at 293 K

| Atom | Site | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|---|
| Cu1 | 4*c* | 0.37582(5) | 0.25 | 0.23622(4) | 77(1) |
| O1 | 4*c* | 0.4913(2) | 0.25 | 0.2344(2) | 102(8) |
| O2 | 4*c* | 0.2610(3) | 0.25 | 0.2399(2) | 119(9) |
| O3 | 4*c* | 0.3788(3) | 0.25 | 0.3624(2) | 120(7) |
| O4 | 4*c* | 0.3733(3) | 0.25 | 0.1098(2) | 119(7) |
| S1 | 4*c* | 0.1321(1) | 0.25 | 0.48519(7) | 133(3) |
| O11 | 4*c* | 0.2007(3) | 0.25 | 0.5512(3) | 288(12) |
| O12 | 4*c* | 0.0506(3) | 0.25 | 0.5306(3) | 270(11) |
| O13 | 8*d* | 0.1380(2) | 0.0800(3) | 0.4272(2) | 186(7) |
| S2 | 4*c* | 0.1265(1) | 0.75 | 0.24303(8) | 112(2) |
| O21 | 4*c* | 0.2036(3) | 0.75 | 0.2975(3) | 236(10) |
| O22 | 8*d* | 0.1246(2) | 0.5819(4) | 0.1845(2) | 255(7) |
| O23 | 4*c* | 0.0541(3) | 0.75 | 0.3029(3) | 239(11) |
| S3 | 4*c* | 0.3838(1) | 0.75 | 0.47739(8) | 197(3) |
| O31 | 4*c* | 0.3984(3) | 0.75 | 0.3794(3) | 340(13) |
| O32 | 8*d* (0.65)[a] | 0.3276(4) | 0.9157(8) | 0.4979(4) | 479(14)[b] |
| O33 | 8*d* (0.35)[a] | 0.4386(9) | 0.9106(15) | 0.5078(8) | 479(14)[b] |
| O34 | 8*d* (0.325)[a] | 0.4542(9) | 0.7927(22) | 0.5289(8) | 664(39)[c] |
| O35 | 8*d* (0.175)[a] | 0.3014(16) | 0.8028(36) | 0.5024(20) | 664(39)[c] |
| Na1 | 4*c* | 0.1188(2) | 0.75 | 0.0119(2) | 384(7) |
| Na2 | 4*c* | 0.1269(2) | 0.25 | 0.2639(2) | 243(5) |
| Na3 | 8*d* | 0.4837(1) | 0.0272(2) | 0.1228(1) | 190(4) |
| Na4 | 8*d* | 0.2757(1) | 0.0217(2) | 0.3527(1) | 183(4) |
| Na5 | 8*d* | 0.4877(1) | 0.0371(3) | 0.3535(1) | 199(4) |
| Na6 | 8*d* | 0.2576(1) | 0.0382(3) | 0.1234(1) | 195(4) |
| Na7 | 4*c* | 0.1347(2) | 0.75 | 0.4599(1) | 290(6) |

[a] Site occupation factors are given in brackets.

[b] Coupled refinement of the anisotropic displacement factors.

[c] Coupled refinement of the isotropic displacement factors, because of the shortest interatomic distances for *d*(O34–O34) and *d*(O35–O35) of less than 40 pm for these split positions.

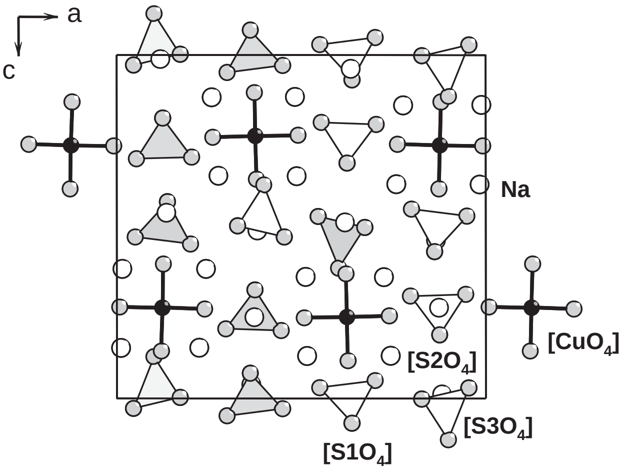

Fig. 1. Projection of the crystal structure of $Na_{11}[CuO_4][SO_4]_3$. Illustrated is only the occupancy of the O32 and O34 sites for $[S3O_4]^{2-}$.

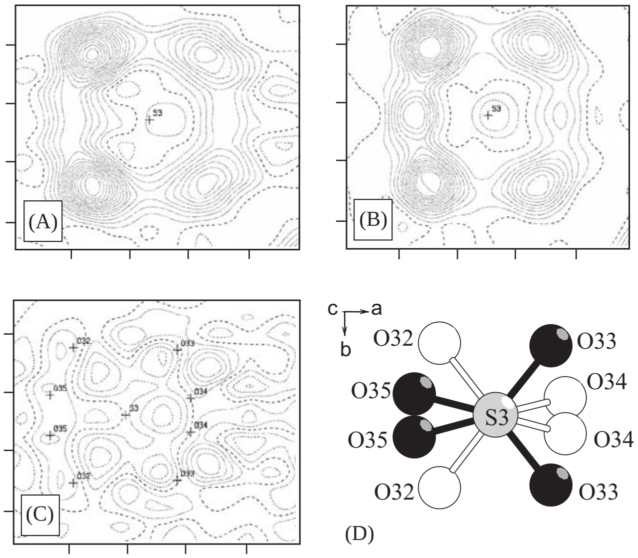

Fig. 2. Difference Fourier maps illustrating the statistical disorder of the $[S3O_4]^{2-}$ anion at 273 K (A) and 170 K (B) without the refinement of O32, O33, O34 and O35 and after the refinement (C). The two orientations of the $[S3O_4]^{2-}$ anion are represented by black (O33 and O35) and white (O32 and O34) circles (D).

crystallographically independent sodium atoms are 6 (Na1), 6 (Na2), 5 (Na3), 6 (Na4), 5 (Na5), 5 (Na6), 5 (Na7) and in the case of O33(2×) and O35: 5 (Na1), 6 (Na2), 5 (Na3), 5 (Na4), 6 (Na5), 5 (Na6), 6 (Na7). Only Na2 and Na3 are not affected by statistical occupancies. For selected interatomic distances and angles at 293 K see Table 3.

The coordination spheres of the isolated anions with sodium cations is illustrated in Fig. 3. For $[CuO_4]^{5-}$ the surrounding polyhedron consisting of sodium cations can be described as a distorted cube-octahedron. A three-fold, four-fold and five-fold capped cube is found for $[S3O_4]^{2-}$, $[S2O_4]^{2-}$ and $[S1O_4]^{2-}$, respectively. In all cases Na4, Na6 and Na3 or Na5, respectively, form a distorted cube, whereas Na1, Na2 and Na7, respectively, are the capping atoms with the limitation of *d*(Na–O) <300 pm being considered for this description. For simplicity reasons one can eliminate the oxygen atoms and derive the principal building block scheme presented in Fig. 4 with a closely to the CsCl-type of structure related arrangement, according to ‘8 CsCl’≡[(Na3, Na4, Na5, Na6)$_2$][Cu, □, S1, S2, S3, Na1, Na2, Na7]. Within the channels along [010] one site is occupied by Cu$^{III}$, whereas the next following is empty (denoted □). All other sites are filled by sodium and sulfur atoms in the following fashion: …S, Na, S, Na,… and in neighboring chains …Na, S, Na, S… so that each sulfur atom site is surrounded only by sodium sites and vice versa.

A Rietveld refinement [12] of the measured X-ray powder diffraction data is given in Fig. 5. The cell parameters derived are $a = 1597.06(6)$ pm, $b = 703.26(3)$ pm, $c = 1481.95(6)$ pm. The atomic parameters and coefficients of the thermal displacement factors have not been refined and have been taken from

Table 3
Interatomic distances (in pm) and angles (in deg) for $Na_{11}[CuO_4][SO_4]_3$ at 293 K

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu–O1 | 184.9(4) | S1–O11 | 147.5(4) | S2–O21 | 147.8(5) | S3$^{a}$–O31 | 148.0(4) |
| Cu–O2 | 184.0(4) | S1–O12 | 146.9(5) | S2–O22 | 147.3(3) | S3–O32 | 150.7(6) |
| Cu–O3 | 188.1(3) | S1–O13 | 148.1(3) | S2–O22 | 147.3(3) | S3–O32 | 150.7(6) |
| Cu–O4 | 188.4(3) | S1–O13 | 148.1(3) | S2–O23 | 146.3(4) | S3–O34 | 140.0(13) |
| | | | | | | S3$^{b}$–O31 | 148.0(4) |
| | | | | | | S3–O33 | 150.3(12) |
| Na1–O3 | 222.7(4) | Na2–O1 | 217.3(5) | Na3–O1 | 229.3(3) | S3–O33 | 150.3(12) |
| Na1–O32 | 251.9(6)$^{a}$ | Na2–O2 | 217.6(5) | Na3–O4 | 237.5(4) | S3–O35 | 142.1(26) |
| Na1–O32 | 251.9(6)$^{a}$ | Na2–O22 | 262.5(3) | Na3–O12 | 245.3(3) | | |
| Na1–O33 | 256.7(10)$^{b}$ | Na2–O22 | 262.5(3) | Na3–O23 | 251.5(3) | Na4–O3 | 231.3(4) |
| Na1–O33 | 256.7(10)$^{b}$ | Na2–O13 | 271.9(3) | Na3–O13 | 260.7(4) | Na4–O2 | 234.1(3) |
| Na1–O34 | 272.3(14)$^{a}$ | Na2–O13 | 271.9(3) | | | Na4–O21 | 238.5(3) |
| Na1–O22 | 283.5(4) | | | | | Na4–O32 | 243.5(7)$^{a}$ |
| Na1–O22 | 283.5(4) | | | | | Na4–O13 | 250.4(4) |
| Na1–O11 | 295.0(6) | | | | | Na4–O35 | 274.4(29)$^{b}$ |
| | | | | | | Na4–O31 | 277.5(4) |
| Na5–O3 | 230.5(4) | Na6–O2 | 229.2(3) | Na7–O4 | 223.8(4) | | |
| Na5–O34 | 232.0(13)$^{a}$ | Na6–O32 | 233.8(7)$^{a}$ | Na7–O13 | 238.0(3) | | |
| Na5–O1 | 232.7(3) | Na6–O35 | 232.5(29)$^{b}$ | Na7–O13 | 238.0(3) | | |
| Na5–O33 | 240.8(13)$^{b}$ | Na6–O4 | 238.9(4) | Na7–O21 | 265.9(5) | | |
| Na5–O22 | 241.6(4) | Na6–O11 | 239.6(3) | Na7–O23 | 267.3(5) | | |
| Na5–O31 | 250.9(3) | Na6–O22 | 246.7(4) | Na7–O35 | 276.9(27)$^{b}$ | | |
| Na5–O33 | 258.9(11)$^{b}$ | Na6–O35 | 276.3(29)$^{b}$ | Na7–O12 | 297.2(6) | | |
| Na5–O34 | 268.2(14)$^{a}$ | | | | | | |
| O1–Cu–O2 | 179.2(2) | O11–S1–O12 | 110.8(3) | O22–S2–O23 | 110.2(2) (2 × ) | | |
| O3–Cu–O2 | 89.78(2) | O13–S1–O12 | 109.0(2) (2 × ) | O21–S2–O23 | 109.1(3) | | |
| O4–Cu–O2 | 90.5(2) | O13–S1–O11 | 110.0(2) (2 × ) | O22–S2–O22 | 107.3(2) | | |
| O1–Cu–O3 | 89.4(2) | O13–S1–O13 | 108.2(2) | O21–S2–O22 | 110.0(2) (2 × ) | | |
| O1–Cu–O4 | 90.4(2) | | | | | | |
| O3–Cu–O4 | 179.8(2) | | | | | | |
| O31–S3$^{a}$–O34 | 114.5(6) | O31–S3$^{b}$–O35 | 113.9(12) | | | | |
| O32–S3$^{a}$–O34 | 122.6(6) | O33–S3$^{b}$–O35 | 105.4(12) | | | | |
| O32–S3$^{a}$–O34 | 101.8(7) | O33–S3$^{b}$–O35 | 131.4(12) | | | | |
| O32–S3$^{a}$–O31 | 107.2(3) (2 × ) | O33–S3$^{b}$–O31 | 101.9(5) (2 × ) | | | | |
| O32–S3$^{a}$–O32 | 101.6(5) | O33–S3$^{b}$–O33 | 97.8(9) | | | | |

Notation concerning the statistical orientation of the $[S3O_4]^{2-}$ anion: [a]Atomic sites O32 (2 × ) and O34 (1 × ) occupied. [b]Atomic sites O33 (2 × ) and O35 (1 × ) occupied.

single-crystal data. Within the limitations of this method and the quality of the data the sample consists of only one phase: $Na_{11}[CuO_4][SO_4]_3$.

### 3.2. MAPLE calculations

The Madelung Part of the Lattice Energy, MAPLE [13], has been calculated for $Na_{11}[CuO_4][SO_4]_3$ paying attention to the two different statistical orientations of the $[S3O_4]$-group. In the case of the occupation of the O32 (2 × ) and O34 (1 × ) sites (A) a MAPLE value of 27846 kcal/mol is obtained, whereas for the other orientation O33 (2 × ) and O35 (1 × ) (B) a MAPLE value of 27721 kcal/mol is calculated. The deviation of these values should be within 1% of the one derived from the binary oxides for a plausible structure solution. Since structural data for '$Cu_2O_3$' is not available, $NaCuO_2$ is used instead. According to $2Na_2O + NaCuO_2 + 3Na_2SO_4 \rightarrow Na_{11}[CuO_4][SO_4]_3$ a pseudo-binary MAPLE value can be derived with 27859 kcal/mol. Comparison of the MAPLE values gives a deviation of 13 kcal/mol or 0.05% for (A) and 138 kcal/mol or 0.5% for (B). These results are in very good agreement in terms of the electrostatic point of view.

### 3.3. Infrared spectroscopy

The infrared spectrum of $Na_{11}[CuO_4][SO_4]_3$ shows a broad anti-symmetrical band at 1107 $cm^{-1}$ and one at 624 $cm^{-1}$ which can be assigned to the $\nu_{as}$ (stretching) and $\delta_{as}$ (deformation) vibration of the sulfate group. The $[S1O_4]^{2-}$ and $[S2O_4]^{2-}$ anions are almost tetrahedral within the standard deviations and therefore should

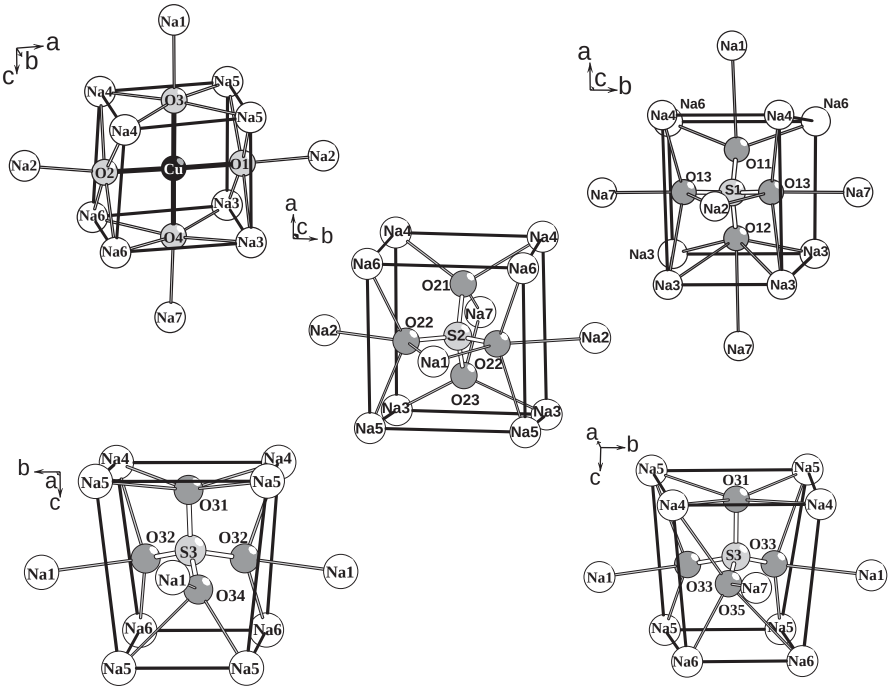

Fig. 3. Coordination spheres of the oxo-anions ($[CuO_4]^{5-}$ and $[SO_4]^{2-}$) in $Na_{11}[CuO_4][SO_4]_3$.

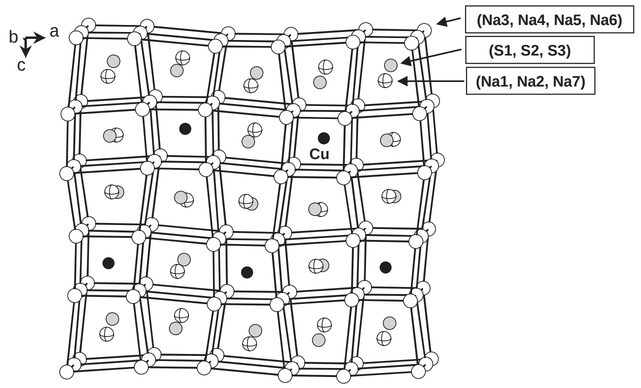

Fig. 4. Illustrates the similarity of the cation arrangement to the CsCl-type of structure. The oxygen atoms are for clarity reasons not included.

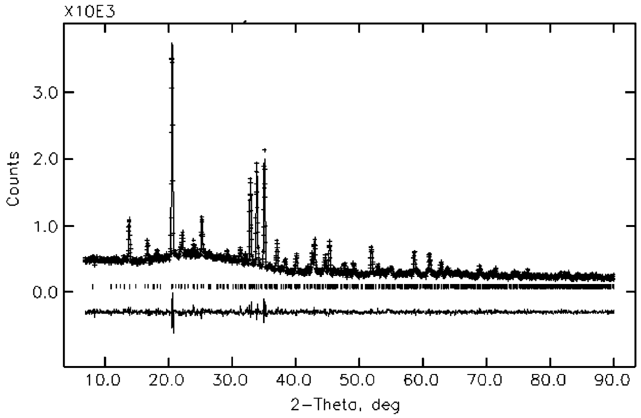

Fig. 5. Rietveld refinement of the X-ray powder data for $Na_{11}[CuO_4][SO_4]_3$.

only show the two allowed vibrations for $T_d$ symmetry, although the site symmetry is lower, which is in accord with the observation. The absence of the $\nu_s$ and $\delta_s$ vibrations is striking, since the $[S3O_4]^{2-}$ anion is far from the tetrahedral arrangement and these vibrations should gain some intensity in the infrared for a lower site symmetry. It may be the case that this anion is also close to $T_d$ symmetry, since the averaged data from X-ray diffraction studies and the derived statistical occupancy of the oxygen atom sites may give a poor picture of the true symmetry.

Similar vibrational data for the 'isolated' $[SO_4]^{2-}$ anion have been reported for $Na_6O(SO_4)_2$ [14] and our results are in good agreement with these.

### 3.4. Absorption spectroscopy

The intense ruby-red color of the crystals of $Na_{11}[CuO_4][SO_4]_3$ originates from the absorption in the 25000–17000 $cm^{-1}$ region of the spectrum. From spectroscopic investigations of the $[Cu(H_2TeO_6)_2]^{5-}$ and $[Cu(HIO_6)_2]^{5-}$ complexes containing square-planar coordinated $Cu^{III}$ [15], it is known that the first ligand to metal charge transfer band is located at $\approx 24000\,cm^{-1}$. For $Ba_4A[CuO_4][CO_3]_2$ with $A = $ Li, Na [16] the charge transfer band is observed at 22000 $cm^{-1}$. Therefore, it seems likely that the origin of the intensity centered at 22000 $cm^{-1}$ is also derived from such a $L \rightarrow M$ charge transfer transition in this case here. The $d-d$ transitions of a $[CuO_4]^{5-}$ complex are of much weaker intensity and would be expected above 19000 cm$^{-1}$ and are not resolved. Some support of this assignment is obtained from the comparison with the absorption spectra of $Cs_4NiSi_2O_7$ and $Cs_6NiSi_2O_8$ [17] containing the square-planar $[NiO_4]$-chromophore ($Ni^{2+}$, $d^8$). For these examples a $d-d$ transition at 17500 cm$^{-1}$ (according to expectations of approximately $2\Delta_0$ with $\Delta_0 = 9000\,\text{cm}^{-1}$ for $[Ni(H_2O)_6]^{2+}$) is observed and the more intense LMCT bands located above 30000 cm$^{-1}$. Both transition metal ions have a $d^8$-configuration, but different oxidation states. It is well known, that the charge transfer bands are lower and the $d-d$ transitions higher in energy for the higher oxidation state, in agreement with the observation for $Na_{11}[CuO_4][SO_4]_3$ here.

### 3.5. EPR measurements

$Na_{11}[CuO_4][SO_4]_3$ should be diamagnetic because of the low-spin $d^8$ configuration of trivalent copper. In order to check for possible oxygen vacancies with the result of divalent copper being present in a non-stoichiometric compound like in superconductors, we carried out EPR measurements at different temperatures, see Fig. 6. At temperatures below 50 K an anisotropic EPR signal (Curie-type behavior) is observed suggesting approximately 1–2% copper in the divalent state (internal standard: ruby). The derived $g$-values at 2 K are: $g_{\|} = 2.37$ and $g_{\perp} = 2.08$ ($g_{av} = 2.18$) are typical for $Cu^{2+}$ in various coordinations, e.g. octahedral, square-planar and square-pyramidal [18], with $g_{\|} = 2.32-2.45$ and $g_{\perp} = 2.07-2.10$ ($g_{av}$= 2.16−2.22). The comparison of our data with the literature suggests that the sample consists of $Na_{11}[CuO_4][SO_4]_3$ with a 1–2% impurity of copper(II) in a presumably square-planar coordination of oxygen, which is consistent with the $g$-values ($g_{\|} = 2.32$ and $g_{\perp} = 2.07$) observed for the mineral Egyptian Blue, $CaCuSi_4O_9$ [19].

### 3.6. Conclusions

With $Na_{11}[CuO_4][SO_4]_3$ the first oxide–sulfate of trivalent copper has been obtained from a redox reaction of CuO and $Na_2O_2$ and has been structurally characterized. So far no single-crystal structure determination of a sodium–oxocuprate(II) and/or –sulfate has been reported and for $Na_6Cu_3O_2(SO_4)_4$ [20] only powder data is available. It is well known that mixtures of $Na_2O$ and CuO give NaCuO and, if the synthesis is carried out in sealed inert containers, $NaCuO_2$ is formed as well. Therefore, we have studied the system $Na_2O$/CuO/$Na_2SO_4$ (molar ratio 4:2:4, $T_{max} = 600°C$) in sealed silver ampoules. From X-ray diffraction analysis the products $Na_5[CuO_2][SO_4]$ [4] and $Na_{11}[CuO_4][SO_4]_3$ have been observed and single crystals of both compounds could be isolated as well. The formation of a phase isotypic to $NaKCu_3O(SO_4)_3$ [6] or $Na_6Cu_3O_2(SO_4)_4$ [20] has not been observed. These investigations of the reactivity within the system $Na_2O$/CuO/$Na_2SO_4$ let us assume that the only two complex phases under the conditions described above are $Na_5[CuO_2][SO_4]$ and $Na_{11}[CuO_4][SO_4]_3$. Therefore, it is very likely that the finding of 1–2% $Cu^{II}$ for the latter

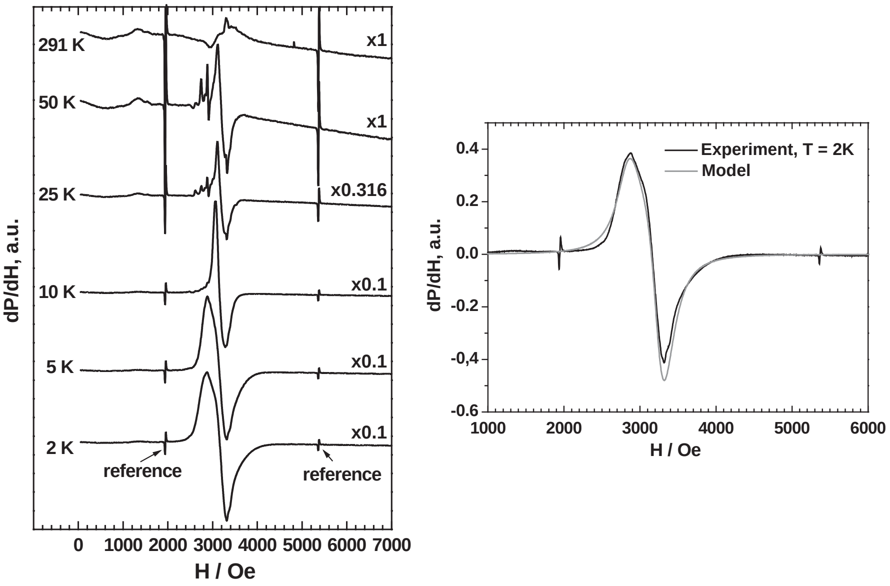

Fig. 6. Temperature dependent EPR measurements with the respective enlargement factors given for each temperature (left) and the simulation ($\nu = 9.477$ GHz, $g_{\|} = 2.37$, $g_{\perp} = 2.08$ and $\Delta H = 230$ Oe) of the spectrum recorded at 2 K (right) for $Na_{11}[CuO_4][SO_4]_3$.

compound (see EPR investigations) is presumably not due to an impurity of a further yet unknown phase.

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