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$Ca_{1-x}CuO_2$, a $NaCuO_2$-Type Related Structure

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The crystal structure of $Ca_{1-x}CuO_2$, a low-temperature phase in the Ca–Cu–O system, has been studied by X-ray diffraction. The structure contains edge-shared chains of CuO_4 squares, forming linear $[CuO_2]$ chains, and is related to the $NaCuO_2$-type. In contrast to the $NaCuO_2$-type, the calcium atoms are not well localized, and various superstructures caused by different Ca ordering are observed. The different superstructures observed are based on a pseudoorthorhombic substructure with lattice constants a = 2.807 (1) Å, b = 6.351 (2) Å, and c = 10.597 (3) Å and space group *Fmmm*.

Introduction

The occurrence of a high-temperature superconducting phase in the SrO–CaO–Bi_2O_3–CuO system[1] has given rise to many papers describing the structure and properties of the superconductor phase. Phase-equilibria data for this important four-component system, however, have been sparse. The ternary SrO–CaO–CuO system has been studied recently, and surprisingly a new binary low-temperature phase with tentative stoichiometry $CaCuO_2$ has been found.[2] This phase, stable up to 760 °C showed different superstructures based on a small orthorhombic unit cell. In the following, the substructure and one particular superstructure of this new phase, $Ca_{1-x}CuO_2$, will be described.

Experimental Section

The new phase $Ca_{1-x}CuO_2$ was prepared in powder and single crystal form.[2] Single-phase powders were obtained by using a citrate route. Dried anhydrous $CaCO_3$ and $CuCO_3$ were dissolved in dilute nitric acid and complexed with excess citric acid monohydrate. After evaporating the excess water, gas evolution was observed while the carbonaceous material oxidized rapidly. The resulting low-density powder was heated to 700 °C in a mullite crucible and then pressed into a pellet and calcined at 700 °C in oxygen for 18–86 h. A starting composition with a Ca:Cu ratio of 45.33:54.67 (0.829) yielded single-phase material, whereas compositions of 45.2:54.8 (0.825) and 45.45:54.55 (0.83) indicated the presence of excess CuO and CaO, respectively.

Red transparent single crystals were grown from a NaCl/KCl flux by slow cooling from 900 to 645 °C at a rate of 1 °C/h. Several of these single crystals of $Ca_{1-x}CuO_2$ were investigated by using a Nonius CAD-4 diffractometer.[3] All calculations for the structure refinement were carried out using the NRCCVAX program package[4] implemented on a MicroVAX I minicomputer. For the least-squares refinement, the block matrix method (all reflections, unit weights) was mostly used since strong correlations were introduced by the higher pseudosymmetry of the small substructure. For the last cycles of refinement, the full-matrix least-squares method was used. The R value for all reflections and unit weights is high (R = 42%), since only 11% of the reflections are observed. The final agreement values were then calculated by using counting statistics weights, giving a lower R value, the contribution of the unobserved reflections being only 0.4%. Experimental details of the structure determination are given in Table I.

Table I. Crystallographic Data

subcell of $Ca_{1-x}CuO_2$	
space group	*Fmmm*
Z	4
a	2.807 (1) Å
b	6.351 (2) Å
c	10.597 (3) Å
V	188 (1) Å^3
radiation	Mo Kα
$2\theta_{max}$	80°
no. of reflns	
measd	1295
unique	184
obsd	183 [$I_{net} \geq 2.5\sigma(I)$]
abs coeff	13.29 mm^{-1}
R_f	0.047
R_w	0.063
Supercell of $Ca_{1-x}CuO_2$	
space group	*Pnca*
Z	20
a	14.035 (3) Å
b	6.351 (2) Å
c	10.597 (3) Å
V	944.6 (4) Å^3
radiation	Mo Kα
$2\theta_{max}$	80°
no. of reflns	
measd	7075
unique	2886
obsd	334 [$I_{net} \geq 2.5\sigma(I)$]
R_f	0.194
R_w	0.123

Table II. Subcell of $Ca_{1-x}CuO_2$

atom	x	y	z	B_{iso}, Å^2
Ca[a]	x	$^1/_4$	$^1/_4$	6.5 (7)
Cu	0	0	0	0.96 (5)
O	$^1/_2$	0	0.1194 (7)	3.8 (5)

[a] Ca: disordered along the a axis: broad maximum at $x = {}^1/_2$.

Results

All crystals studied displayed the same common pseudoorthorhombic subcell with a = 2.807 Å, b = 6.351 Å, c = 10.597 Å, and space group *Fmmm*. The substructure reflections were measured, and a refinement was carried out. Results are listed in Table II. The structure contains well-localized $[CuO_2]$ chains that produce channels parallel to the a axis. In Fourier maps, a nearly uniform string of electron density was observed within these channels, indicating a one-dimensional superstructure. The calcium atoms in the channels, therefore, are randomly disordered, and the superstructures are likely caused by calcium ordering and variations in the calcium stoichiometry.

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Table III. Superstructure Cell of $Ca_4Cu_5O_{10}$[a]

atom	x	y	z	B_{iso}, Å^2
Cu1	0.6488 (2)	−0.0111 (4)	0.2562 (3)	0.49 (3)
Cu2	0.0509 (2)	0.0077 (4)	0.2474 (3)	0.46 (3)
Cu3	0.25	0	0.2502 (4)	0.98 (5)
Ca1	0.0606 (6)	0.253 (2)	0.0041 (8)	2.41 (11)
Ca2	0.3143 (8)	0.252 (2)	0.0011 (9)	3.56 (17)
O1	0.149 (2)	−0.025 (5)	0.128 (3)	2.37
O2	0.947 (2)	0.023 (5)	0.130 (3)	2.37
O3	0.454 (2)	0.461 (5)	0.130 (3)	2.37
O4	0.652 (2)	0.446 (5)	0.128 (3)	2.37
O5	0.25	0.5	0.135 (4)	2.37
O6	0.75	0	0.134 (4)	2.37

[a] The temperature factors for the oxygen atoms were fixed at 2.37 Å^2.

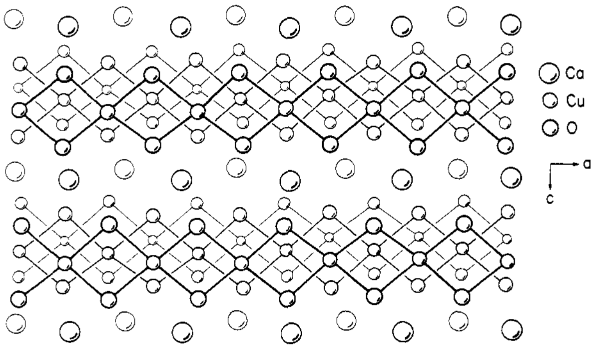

Figure 1. View of the $Ca_{1-x}CuO_2$ structure.

Several different supercells with a 10- or 12-fold a axis were identified from Bürger precession photographs and reported earlier.[2] In one particular crystal, a simple superstructure with only a 5-fold a axis was found and subsequently investigated. The superstructure reflections were measured for a primitive unit cell with $a' = 5a = 14.035$ Å, $b = 6.351$ Å, and $c = 10.597$ Å. The space group consistent with the observed extinction rules was *Pnca*; however, a weakly violated *B* centering was also found, indicating a possible higher pseudosymmetry. A difference Patterson map (Patterson symmetry *Pmmm*, superstructure reflections only) showed a strong peak consistent with a Ca–Ca spacing of roughly 3.46 Å. The ratio of the Cu–Cu to Ca–Ca distance is roughly 4/5, suggesting a nearly 5-fold superstructure along the a axis. The stoichiometry then becomes $Ca_4Cu_5O_{10}$, since on average four calcium atoms fit over five copper atoms. With this information, the superstructure was successfully refined in space group *Pnca*, yielding a stoichiometry of $Ca_{0.8}CuO_2$. Table III gives the refined superstructure atom positions, and Table IV lists interatomic distances; Figure 1 shows a view of the structure down the b axis. To reduce the number of variables, the oxygen thermal parameters were all fixed at $B = 2.37$ Å^2, a value slightly larger than the overall temperature parameter derived from the Wilson plot. A final difference Fourier map showed small residual peaks between the $[CuO_2]$ chains along the a axis in positions suitable to accommodate a calcium atom; however, the distances between the calcium atoms and these peaks were too short. Therefore, some degree of disorder of the calcium atoms in the channels is still present.

Table IV. Interatomic Distances in $Ca_{1-x}CuO_2$ (Superstructure)[a]

Ca1–O4	2.26 (3)	Ca2–O1	2.04 (3)
Ca1–O2	2.26 (3)	Ca2–O5	2.30 (3)
Ca1–O3	2.27 (3)	Ca2–O6	2.33 (3)
Ca1–O3	2.46 (3)	Ca2–O4	2.41 (3)
Ca1–O1	2.53 (3)	Ca2–O3	2.73 (3)
Ca1–O2	2.54 (3)	Ca2–O2	2.74 (3)
Ca1–Ca2	3.46 (2)	Ca2–Ca1	3.46 (2)
Ca1–Ca2	3.56 (2)	Ca2–Ca1	3.56 (2)
Ca1–Ca1	3.57 (2)	Ca2–Ca1	3.60 (2)
Ca1–Ca2	3.60 (2)	Ca2–Ca2	3.63 (3)
Ca1–Ca1	3.63 (2)	Ca2–Ca1	3.65 (2)
Ca1–Ca2	3.65 (2)	Ca2–Ca2	3.67 (3)
Cu1–O5	1.83 (3)	Cu2–O1	1.88 (3)
Cu1–O3	1.88 (3)	Cu2–O3	1.89 (3)
Cu1–O2	1.90 (3)	Cu2–O2	1.92 (3)
Cu1–O6	1.92 (3)	Cu2–O4	1.96 (3)
Cu1–Cu2	2.804 (4)	Cu2–Cu3	2.796 (3)
Cu1–Cu1	2.844 (6)	Cu2–Cu1	2.804 (4)
Cu3–O1	1.92 (3) 2×		
Cu3–O4	1.92 (3) 2×		
Cu3–Cu2	2.796 (3) 2×		

[a] All distances are given in Å [=10^{-1} nm].

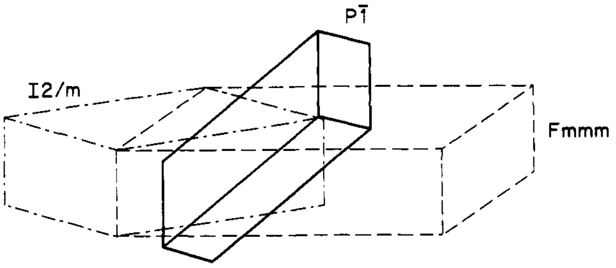

Figure 2. Relationship of the various unit cells: $P\bar{1}$, original unit cell of $NaCuO_2$; $I2/m$, proposed monoclinic unit cell; *Fmmm*, pseudoorthorhombic unit cell.

Discussion

The observed structural feature, $[CuO_2]$ chains forming channels, is common to the $ACuO_2$ phases where A is an alkali metal.[5,6] Different arrangements of the chains give either an octahedral oxygen coordination or trigonal prismatic oxygen coordination for the alkali metals. In all cases, the alkali-metal coordination number is 6, with the larger alkali metals preferring the trigonal prism, whereas only sodium is found in the octahedral site. The close resemblance of $NaCuO_2$ to $Ca_{1-x}CuO_2$ is immediately confirmed since the triclinic unit cell of $NaCuO_2$[5] can be described as pseudoorthorhombic, *F* centered, with $a = 2.748$ Å, $b = 6.354$ Å, and $c = 10.491$ Å, as shown in Figure 2. In $NaCuO_2$, however, all the edge-sharing octahedra produced by the $[CuO_2]$ chains are occupied by sodium atoms, resulting in short Na–Na contacts of 2.75 Å. In contrast, the calcium ion has roughly the same radius but twice the charge, and therefore a longer Ca–Ca separation is expected. Indeed, it is not possible to pack calcium atoms closer than roughly 3.2 Å as is seen for instance in $Ca_{0.85}Sr_{0.15}CuO_2$, Ca_2CuO_3, and $CaCu_2O_3$, where the closest Ca–Ca distances vary from 3.2 to 3.5 Å.[7-9] In analogy to $NaCuO_2$, an octahedral oxygen coordination for calcium is expected in $Ca_{1-x}CuO_2$, although with larger distortions. In the superstructure, the two independent calcium atoms occupy distorted octahedra, with average Ca–O distances of 2.38 and 2.42 Å, values that compare well with distances found in other compounds, such as $Ca_{0.85}Sr_{0.15}CuO_2$ and Ca_2CuO_3.[7,8] The $[CuO_2]$ chains are slightly modulated; four

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Table V. $NaCuO_2$[a]

atom	x	y	z
Na	0	$^1/_2$	$^1/_2$
Cu	0	0	0
O	0.345	0	0.575

[a] Monoclinic unit cell, space group $I2/m$, $Z = 2$, $a = 6.160$ (4) Å, $b = 2.747$ (2) Å, $c = 6.105$ (4) Å, and $\beta = 117.62$ (3)°.

shorter Cu–Cu distances of roughly 2.8 Å alternate with one longer distance of 2.84 Å. The Cu–O distances are within the expected range and vary from 1.83 to 1.96 Å.

The variety of different superstuctures observed in $Ca_{1-x}CuO_2$[2] suggests structural phase transitions due to ordering of calcium atoms on cooling from the growth temperature. At high temperature, the calcium atoms are disordered in the channels parallel to the a axis, the symmetry of the lattice being orthorhombic. On cooling, ordering of the calcium atoms sets in, but different superstructures may develop, depending on calcium stoichiometry, cooling rate, temperature gradient, oxygen partial pressure, etc., accounting for the variety of observed superstructures. For instance, the preparation method clearly affects the stoichiometry, where flux grown crystals show a calcium to copper ratio of 0.8, whereas single-phase powders obtained in an oxygen atmosphere show a ratio of 0.829. The difference in growth temperatures and oxygen partial pressure may account for this.

Comparing $Ca_{1-x}CuO_2$ to $NaCuO_2$, one notices that the average copper valence is reduced from Cu^{3+} in $NaCuO_2$ to $Cu^{2.4+}$ in $Ca_{1-x}CuO_2$. To account for the insulating properties of $Ca_{1-x}CuO_2$, a mixed copper valence may be assumed, giving $Ca_4Cu^{2+}{}_3Cu^{3+}{}_2O_{10}$. The presence of Cu^{3+} is consistent with the fact that the phase becomes unstable at higher temperatures, although its stability range exceeds that of $NaCuO_2$. Appropriate doping to stabilize Cu^{2+} should extend the stability range even further.

The unit cell of $NaCuO_2$ as determined from Guinier powder X-ray patterns[5] was found to be triclinic with $a = 2.748$ Å, $b = 6.671$ Å, $c = 3.462$, $\alpha = 76.2°$, $\beta = 113.4°$, and $\gamma = 128.1°$. This triclinic cell is pseudoorthorhombic as given above, and an attempt to index the given powder pattern indicated line splittings consistent with monoclinic symmetry, resulting in an I-centered unit cell with $a = 6.160$ Å, $b = 2.748$ Å, $c = 6.105$ Å, and $\beta = 117.62°$ (see Figure 2). The powder pattern for $NaCuO_2$ calculated by using this monoclinic unit cell, space group $I2/m$, and transformed atom coordinates matches the observed intensities. It is therefore suggested that $NaCuO_2$ is monoclinic, and, similar to $Ca_{1-x}CuO_2$, undergoes a structural phase transition from monoclinic to orthorhombic at high temperature. The transformed unit-cell parameters and atom coordinates are given in Table V.

Summary

In summary, we have shown that the crystal structure of $Ca_{1-x}CuO_2$ is related to the $NaCuO_2$-type structure. Linear $[CuO_2]$ chains form channels with calcium atoms disordered at high temperatures and ordered at lower temperatures. Different superstructures caused by calcium ordering may develop, depending on the cooling rate, temperature gradient, stoichiometry, etc. Because of the close relation between $Ca_{1-x}CuO_2$ and $NaCuO_2$, sodium doping of $Ca_{1-x}CuO_2$ should be possible to obtain a conducting phase. Different superstructures, commensurate as well as incommensurate, are expected for different doping levels, and charge density wave behavior may occur.

Note Added in Proof. A recent neutron investigation of $NaCuO_2$ by N. E. Brese et al. (*J. Solid State Chem.* **1989**, *83*, 1) established the monoclinic symmetry of the unit cell.

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Registry No. $CaCuO_2$, 57348-56-8; $Ca_{0.8}CuO_2$, 125648-48-8; $NaCuO_2$, 12174-73-1.

Supplementary Material Available: Listings of distances and bond angles (6 pages); listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of $Cu_2ZnGeS_{4-y}Se_y$

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Cu_2ZnGeS_4 can be prepared in both tetragonal stannite and orthorhombic wurtz–stannite phases, whereas $Cu_2ZnGeSe_4$ exists only in the tetragonal phase. Selenium can be substituted for sulfur up to 100% in the tetragonal structure of $Cu_2ZnGeS_{4-y}Se_y$ prepared at 700 °C and up to 75% in the orthorhombic structure prepared at 900 °C. The temperature at which the phase transformation takes place was found to increase with higher selenium concentration. Iron was substituted into both forms of $Cu_2Zn_{1-x}Fe_xGeS_{4-y}Se_y$, and the resulting magnetic properties indicated that the Fe–Fe superexchange interactions are the same in both structures.

Introduction

In recent years, ternary chalcopyrites and quaternary chalcogenides have been studied to observe their semiconducting and optical properties. Some of them are promising for nonlinear optics.[1] Quaternary chalcogenides having the formula $Cu^I{}_2B^{II}C^{IV}X_4$, where B^{II} = Mn, Fe, Co, Ni, and Zn, have been prepared and characterized previously.[2-5]

These chalcogenides form a large class of structurally related compounds. Their structure is derived from the

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