Structure and Oxidation State Relationships in Ternary Copper Oxides

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Powder neutron diffraction has been used to determine accurate oxygen positions in five simple ternary copper(II) oxides, $SrCuO_2$, Sr_2CuO_3, Bi_2CuO_4, Ca_2CuO_3, and Li_2CuO_2. These materials have structures based on corner- or edge-sharing CuO_4 square planes with Cu–O distances between 1.907 and 2.04 Å. In $KCuO_2$ the CuO_4 square planes are distorted with two short copper oxygen bonds of 1.81 Å. The structures of the more complex materials $BaCuO_{2+x}$ ($x = 0, 0.07$) have also been studied using powder neutron diffraction techniques and the oxygen distribution in these materials was examined. Variations in copper(II) and copper(III) geometries are interpreted in terms of bond valence calculations which have been carried out for all the materials studied. © 1989 Academic Press, Inc.

Introduction

The oxide chemistry of copper, in particular that of the 2+ and 3+ states, has recently commanded much attention in relation to studies of high-temperature superconductors (*1–3*). However, the structural chemistry of copper 2+ and 3+ in oxides outside of these perovskite-based materials is largely uninvestigated. In particular many binary compounds of copper oxides with heavy metal oxides have only been studied by X-ray methods leading to poorly defined oxygen positions and inaccurate bond lengths. The use by many authors of bond valence calculations (*4*) to determine site oxidation states in superconducting phases (*2, 3*) depends very much on the use of accurate copper oxygen distances for the derived parameters.

A notable feature of the 123-type high-temperature superconductors is the need to anneal them in oxygen at approximately 400°C to ensure an average copper oxidation state near 2.33; this mixed oxidation level seems necessary for the observation of superconductivity (*3*). In the bismuth- and thallium-based materials a high oxidation state seems to be controlled by the proportions of trivalent and bivalent cations. The synthesis of many complex copper oxides containing Cu^{3+}, e.g., $MCuO_2$ (*5*) and $Li_3Cu_2O_4$ (*6*), requires heating the reactants under oxygen at approximately 400°C.

The oxygen stoichiometry of $BaCuO_{2+x}$ can also be controlled by thermal treatments with various oxygen partial pressures again at approximately 400°C (*7*). Barium copper oxide prepared in air or pure oxygen at high temperatures, e.g., 800°C, and cooled rapidly to room temperature has a stoichiometry of approximately

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$BaCuO_{2.10}$; by annealing this material under vacuum at 400°C a stoichiometric material may be prepared. Kipka and Muller-Buschbaum (8) have determined the structure of $BaCuO_2$ by single-crystal X-ray methods. The unit cell is cubic with a lattice constant, slightly dependent on oxygen stoichiometry, of 18.27 Å. The complex structure contains various coordination environments for both barium and copper. Some of these sites are only partially occupied and Migeon et al. (7) have suggested that the excess oxygen could be incorporated into the structure on such positions.

We have refined the structures of $SrCuO_2$, Sr_2CuO_3, Ca_2CuO_3, Bi_2CuO_4, Li_2CuO_2, $KCuO_2$, $BaCuO_2$, and $BaCuO_{2.07}$ using a full-profile powder neutron diffraction method in order to determine accurate oxygen positions and hence the validity of bond valence calculations for these complex oxides.

Experimental

The stoichiometric materials were synthesized by direct reaction of CuO (99.999%) with metal oxides or carbonates in alumina crucibles as summarized in Table I. Mixtures were reground frequently during the reaction period and, in most cases, finally quenched to room temperature. Bi_2CuO_4 was isolated by the slow cooling of the molten mixture to room temperature.

The barium copper oxide was analyzed thermogravimetrically using a Stanton Redcroft TG1000 system. Samples were heated to 800°C under N_2 + 5% H_2 at 30°/min resulting in reduction to BaO and copper metal. Weight loss in the region gave the compositions of the air-quenched material as $BaCuO_{2.08\pm0.02}$. A portion of the original material was heated at 400°C under vacuum for 24 hr and reanalyzed gravimetrically to give a composition $BaCuO_{2.00\pm0.02}$.

TABLE I

Oxide	Reactants	Temp. (°C)	Time (days)	Atmosphere	Ref.
$SrCuO_2$	$SrCO_3$ + CuO	850	8	Air	(14)
Sr_2CuO_3	$SrCO_3$ + CuO	850	8	Air	(16)
Ca_2CuO_3	$CaCO_3$ + CuO	800, 850	1, 8	Air	(14)
Li_2CuO_2	Li_2CO_3 + CuO	760	2	Air	(19)
Bi_2CuO_4	Bi_2O_3 + CuO	750	3	Air	(17)
$KCuO_2$	KO_2 + CuO	425	2	O_2	(5)
$BaCuO_{2.07}$	BaO + CuO	800	4	Air	(8)
$BaCuO_{2.00}$	$BaCuO_{2.07}$	400	1	Vacuo	(8)

Powder X-ray diffraction patterns were recorded using an INEL position-sensitive detector-based system. All the materials were shown to be single phase except Bi_2CuO_4, the diffraction pattern of which showed evidence for a very small fraction of Bi_2O_3.

Powder neutron diffraction patterns were collected using the high-resolution powder diffractometer D2B at the ILL, Grenoble (9), in high-flux mode (strontium, barium, and bismuth copper oxides) and on POLARIS (10) on ISIS at the Rutherford Appleton Laboratory (calcium, lithium, and potassium copper oxides). Samples, between 5 and 30 g, were loaded into vanadium cans and data were collected at room temperature over periods of typically 4–8 hr. Refinements were carried out using the Rietveld full-profile method (11) using a version of the program (12) running on the IBM 3090 at Southampton for the single wavelength data or a code for time-of-flight data operating at the Rutherford Laboratory (13).

Structure Refinements

SrCuO₂

The single-crystal positions given by Teske and Muller-Buschbaum (*14*) in the space group *Cmcm* were used as the basis of the model for the refinement. Scattering lengths were taken from Koester and Yelon (*15*) as Sr 0.690, Cu 0.7689, and O 0.583 fm. Initial stages of the refinement included the profile parameters (zeropoint, halfwidths, lattice constants, and scale factor). Refinement of the atomic positions resulted in some small shifts from the X-ray-determined positions and the final stages of the refinement included anisotropic temperature factors. Final atomic positions, temperature factors, and lattice constants are summarized in Table IIa.

Sr₂CuO₃

Single-crystal X-ray refined positions were taken from Teske and Muller-Buschbaum (*16*) and the refinement was carried out in the stages described above in the

TABLE IIa

SrCuO₂ REFINED ATOMIC COORDINATES

Cmcm
$a = 3.5766(1)$, $b = 16.3354(4)$, $c = 3.9143(1)$ Å

	x	y	z			
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu 4(c)	0.0	0.0608(1)	0.25			
	0.85(6)	0.66(5)	0.53(6)	0.0	0.0	0.0
Sr 4(c)	0.0	0.3313(1)	0.25			
	1.26(7)	0.27(5)	0.38(6)	0.0	0.0	0.0
O1 4(c)	0.0	0.9441(1)	0.25			
	1.46(9)	0.53(7)	0.55(8)	0.0	0.0	0.0
O2 4(c)	0.0	0.1791(1)	0.25			
	1.39(9)	0.51(8)	0.71(9)	0.0	0.0	0.0
		$\chi^{2a} = 2.34$				

$^a \chi = R_{wp}/R_{exp}$. $R_{wp} = \{w_i[y_i(obs) - y_i(calc)]^2/ w_iy_i^2(obs)\}^{1/2}$. $R_{exp} = \{[N - P + C]/w_iy_i^2(obs)\}^{1/2}$, where N, P, and C are the number of observations, parameters, and constraints, respectively.

TABLE IIb

Sr₂CuO₃ REFINED ATOMIC COORDINATES

Immm
$a = 12.7163(2)$, $b = 3.9159(1)$, $c = 3.5032(1)$ Å

	x	y	z			
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu 2(d)	0.5	0.0	0.5			
	0.56(5)	0.43(6)	0.72(6)	0.0	0.0	0.0
Sr 4(f)	0.3521(1)	0.5	0.0			
	0.51(4)	0.51(4)	0.67(4)	0.0	0.0	0.0
O1 4(f)	0.1547(1)	0.5	0.0			
	0.54(5)	0.67(4)	0.88(5)	0.0	0.0	0.0
O2 2(a)	0.0	0.0	0.0			
	0.74(7)	0.58(7)	0.77(7)	0.0	0.0	0.0
		$\chi^{2a} = 2.85$				

^{a} See footnote to Table IIa.

space group *Immm*. The refined data is summarized in Table IIb.

Bi₂CuO₄

The crystal structure of Bi₂CuO₄ has been investigated by Boivin *et al.* (*17*) and Arpe and Muller-Buschbaum (*18*). Both groups indexed the diffraction data on a unit cell of approximate dimensions of $a = b = 8.5$ Å and $c = 5.8$ Å but used two different space groups for the refinement. The material prepared in this work crystallized with a tetragonal unit cell with all peaks indexable in the space group *P4/ncc* used by Boivin *et al.* Attempts to refine the neutron data using the crystallographic information given by Arpe and Muller-Buschbaum were unsuccessful. The refined atomic positions are given in Table IIc.

Ca₂CuO₃

Ca₂CuO₃ crystallizes with the same structure as the strontium analog but with a 15% smaller unit cell. Initial data for the refinement was taken from Teske and Muller-Buschbaum (*14*). The quality of the neutron data for this sample (obtained on PO-

TABLE IIc

Bi$_2$CuO$_4$ Refined Atomic Coordinates

	$P4/ncc$ $a = 8.5063(1)$, $b = 8.5063(1)$, $c = 5.8222(1)$ Å					
	x	y	z			
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu 4(c)	0.0	0.5	0.0782(4)			
	0.32(4)	0.32(4)	0.80(7)	0.0	0.0	0.0
Bi 8(f)	0.1686(1)	0.1686(1)	0.25			
	0.42(3)	0.42(3)	0.84(6)	−0.22(5)	0.19(15)	0.19(15)
O 16(g)	0.2995(2)	0.1075(2)	0.9089(3)			
	0.59(7)	0.80(7)	1.39(5)	0.12(4)	0.19(5)	0.12(5)
		$\chi^{2a} = 2.91$				

^{a} See footnote to Table IIa.

TABLE IIe

Li$_2$CuO$_2$ Refined Atomic Coordinates

	$Immm$ $a = 3.654(2)$, $b = 2.857(2)$, $c = 9.372(6)$ Å			
	x	y	z	B_{eq}
Cu 2(b)	0.0	0.5	0.5	0.02(4)
Li 4(j)	0.5	0.0	0.2892(15)	1.53(16)
O 4(i)	0.0	0.0	0.3576(3)	0.38(5)
		$R_{wp} = 6.66$		

LARIS at the Rutherford Laboratory) was not thought to be of a sufficiently high standard to enable anisotropic temperature factors to be introduced into the refinement. Therefore for this oxide (and also for the oxides KCuO$_2$ and Li$_2$CuO$_2$) the refinement was carried out using isotropic temperature factors only. Final refined atomic positions obtained from the neutron diffraction data are given in Table IId.

Li$_2$CuO$_2$

The refinement was carried out in the space group $Immm$ described by Hoppe and Rieck (19). No correction was made for absorption by lithium and this is reflected in the low-temperature factors obtained for copper and oxygen. Final refined structural parameters are given in Table IIe.

KCuO$_2$

The refinement was based on the single-crystal X-ray structure described by Hestermann and Hoppe (5) in the space group $Cmcm$. This study refined the oxygen on the 8f site (0, y, z) with $z = 0.0$; attempts to refine the z coordinate away from 0.0 resulted in an oscillation about this position. This parameter was therefore set to 0.0. Final atomic and thermal parameters are summarized in Table IIf.

BaCuO$_{2.00}$ and BaCuO$_{2.07}$

The structure of BaCuO$_2$ was originally investigated using single-crystal X-ray methods by Kipka and Muller-Buschbaum (8). We recently studied the structure of this compound at two different oxygen stoi-

TABLE IId

Ca$_2$CuO$_3$ Refined Atomic Coordinates

	$Immm$ $a = 12.208(6)$, $b = 3.768(2)$, $c = 3.249(2)$ Å			
	x	y	z	B_{eq}
Cu 2(d)	0.5	0.0	0.5	0.66(4)
Sr 4(f)	0.3480(3)	0.5	0.0	0.73(4)
O1 4(f)	0.1605(2)	0.5	0.0	0.80(5)
O2 2(a)	0.0	0.0	0.0	0.67(6)
		$R_{wp} = 8.44$		

TABLE IIf

KCuO$_2$ Refined Atomic Coordinates

	$Cmcm$ $a = 4.375(3)$, $b = 11.699(7)$, $c = 5.417(3)$ Å			
	x	y	z	B_{eq}
Cu 4(c)	0.0	0.0059(4)	0.25	0.84(5)
K 4(c)	0.0	0.3005(5)	0.25	0.52(6)
O 8(f)	0.0	0.1049(2)	0.00	0.79(5)
		$R_{wp} = 4.57$		

chiometries by powder neutron diffraction (20).

The data for $BaCuO_{2.07}$ were refined using the single-crystal data of Kipka and Muller-Buschbaum as an initial model in the $Im\bar{3}m$ space group. Attempts to refine a temperature factor for the barium atom at the origin produced an unreasonably high value indicating that this site is in fact vacant; the barium atom was therefore removed from this position. Given the unusual coordination geometry for a barium atom on this site and very long Ba–O interactions, which result in a weakly bonded atom, nonoccupation of this site is not surprising. The excess oxygen above two in $BaCuO_{2+x}$ was located by refining the oxygen(6) site occupancy which is only a partially occupied site in the X-ray structure determination of $BaCuO_{2.00}$. This gave an overall unit cell composition of $Ba_{88}Cu_{90}O_{186}$ or $Ba_{0.98}CuO_{2.07}$ in good agreement with the thermogravimetric analysis. As both Cu(4) and O(6) sites are partially occupied it is worth noting that the refined positions given in Table IIg represent *an average* unit cell.

The data for $BaCuO_{2.00}$ were successfully refined using the same model and a number of small shifts in atomic positions were found. No evidence was found for occupation of the origin site by barium and refinement of the O(6) occupancy gave a unit cell composition of $Ba_{0.98}CuO_{2.00}$. The final atomic positions are summarized in Table IIh.

Results and Discussion

In all cases small discrepancies were observed between the single-crystal X-ray studies and this neutron work. In general the esd's associated with the oxygen positions in this study were a factor of approximately 10 below those from the X-ray data. Small shifts in oxygen sites resulted in differences between the copper oxygen bond

TABLE IIg

$BaCuO_{2.07}$ REFINED ATOMIC COORDINATES

		$Im\bar{3}m$ $a = b = c = 18.2865(4)$ Å			
		x	y	z	Occupancy
Cu1	48(i)	0.1490(1)	0.6490(1)	0.25	1
Cu2	24(h)	0.0	0.1243(1)	0.1243(1)	1
Cu3	12(e)	0.1995(3)	0.0	0.0	1
Cu4	12(e)	0.4384(5)	0.0	0.0	0.5
Ba1	48(j)	0.0	0.1512(2)	0.3151(2)	1
Ba2	24(h)	0.0	0.3624(2)	0.3624(2)	1
Ba3	16(f)	0.1770(2)	0.1770(2)	0.1770(2)	1
O1	48(k)	0.0748(2)	0.0748(2)	0.1868(2)	1
O2	48(k)	0.1442(2)	0.1442(2)	0.3487(2)	1
O3	48(k)	0.2675(2)	0.2675(2)	0.0846(2)	1
O4	12(d)	0.25	0.0	0.5	1
O5	12(e)	0.3329(5)	0.0	0.0	1
O6	48(j)	0.0	0.1160(8)	0.4501(5)	0.379(1)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu1	2.4(2)	2.4(2)	4.2(3)	1.6(1)	3.7(3)	3.7(3)
Cu2	1.6(1)	2.1(1)	2.1(1)	0	0	−1.2(1)
Cu3	0.4(1)	4.6(3)	4.6(3)	0	0	0
Cu4	0.1(3)	3.9(5)	3.9(5)	0	0	0
Ba1	1.3(1)	3.3(2)	2.8(1)	0	0	−0.5(1)
Ba2	7.1(5)	0.8(2)	0.8(2)	0	0	−0.8(2)
Ba3	2.6(2)	2.6(2)	2.6(2)	−0.4(1)	−0.4(1)	−0.4(1)
O1	2.8(2)	2.8(2)	0.7(1)	1.5(1)	−0.2(1)	−0.2(1)
O2	2.6(2)	2.6(2)	2.8(2)	1.5(1)	0.5(1)	0.5(1)
O3	2.2(2)	2.2(2)	2.1(2)	−0.2(1)	0.8(1)	0.8(1)
O4	4.3(5)	0.6(2)	0.6(2)	0	0	0
O5	5.9(5)	2.6(2)	2.6(2)	0	0	0
O6	1.0(5)	8.0(9)	2.1(5)	0	0	3.1(5)

$$\chi^{2a} = 12.78$$

[a] See footnote to Table IIa.

lengths evaluated in this work and those obtained in the X-ray studies of up to 0.1 Å. The copper oxygen bond distances and bond angles determined are summarized in Tables IIIa and IIIb. In all the copper(II) ternary oxides except "$BaCuO_2$" the copper environment is square planar with only small distortions from four identical bond lengths. All the copper oxygen distances for these materials lie in the range 1.88–1.97 Å.

For $KCuO_2$, refinement of the oxygen position produced an elongated square planar environment for copper with two short Cu–O distances of 1.81 Å and two slightly longer bonds of 1.83 Å.

TABLE IIh

$BaCuO_{2.00}$ REFINED ATOMIC COORDINATES

$Im\bar{3}m$
$a = b = c = 18.2772(2)$ Å

	x	y	z	Occupancy
Cu1 48(i)	0.1492(1)	0.6492(1)	0.25	1
Cu2 24(h)	0.0	0.1256(1)	0.1256(1)	1
Cu3 12(e)	0.2031(2)	0.0	0.0	1
Cu4 12(e)	0.4331(2)	0.0	0.0	0.5
Ba1 48(j)	0.0	0.1512(2)	0.3106(2)	1
Ba2 24(h)	0.0	0.3624(1)	0.3624(1)	1
Ba3 16(f)	0.1782(2)	0.1782(2)	0.1782(2)	1
O1 48(k)	0.0741(1)	0.0741(1)	0.1859(1)	1
O2 48(k)	0.1432(1)	0.1432(1)	0.3494(1)	1
O3 48(k)	0.2662(1)	0.2662(1)	0.0845(1)	1
O4 12(d)	0.25	0.0	0.5	1
O5 12(e)	0.3348(3)	0.0	0.0	1
O6 48(j)	0.0	0.1052(6)	0.4497(6)	0.25

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu1	1.1(1)	1.1(1)	1.8(1)	0.3(1)	1.6(2)	1.6(2)
Cu2	0.5(1)	1.7(1)	1.7(1)	0	0	0.1(1)
Cu3	1.7(2)	1.1(1)	1.1(1)	0	0	0
Cu4	0.1(4)	2.1(3)	2.1(3)	0	0	0
Ba1	0.3(1)	1.2(1)	2.4(1)	0	0	-0.8(5)
Ba2	0.7(2)	2.0(2)	2.0(2)	0	0	-0.6(1)
Ba3	1.5(1)	1.5(1)	1.5(1)	0.4(1)	0.4(1)	0.4(1)
O1	1.4(1)	1.4(1)	0.8(1)	0.2(1)	0.3(1)	0.3(1)
O2	1.4(1)	1.4(1)	1.8(1)	0.5(1)	0.0(1)	0.0(1)
O3	1.4(1)	1.4(1)	0.5(1)	-0.4(1)	0.1(1)	0.1(1)
O4	3.6(3)	1.4(2)	1.4(2)	0	0	0
O5	0.9(2)	2.5(2)	2.5(2)	0	0	0
O6	1.0(5)	3.0(8)	2.3(5)	0	0	-4.5(5)

$$\chi^{2a} = 9.15$$

^{a} See footnote to Table IIa.

The refined positions for $BaCuO_{2.00}$ and $BaCuO_{2.07}$ are in general very similar. However, notable shifts (equivalent to a distance of approximately 0.1 Å) occur for the Cu(4) x coordinate, O(6) y coordinate, and the Ba(1) z coordinate. These motions may be easily interpreted in terms of incorporation of excess oxygen onto the O(6) site in $BaCuO_{2.07}$. Of the four O(6) sites surrounding Cu(4) in $BaCuO_{2.00}$ only two are filled on average. Assuming these lie opposite one another the copper coordination is approximately trigonal with a short Cu(4)–O(5) bond. This geometry is frequently found for Cu^+ in solids. The incorporation of the extra oxygen to give $BaCuO_{2.07}$ changes the coordination geometry to approximately square planar with the further occupation of the O(6) site. The Cu(4)–O(5) bond elongates considerably to give a copper coordination geometry common in Cu^{2+} and Cu^{3+} chemistry. Ba(1) also shifts in association with the greater occupancy of the O(6) site demonstrating a greater interaction.

The bond valence theory of Brown (4) has been extensively to relate metal oxidation levels to coordination environments in solids. Recently this theory has been employed to probe the copper oxidation state in various sites in high-temperature superconductors (2, 3) in order to locate the most likely positions for the, formally, Cu^{3+} ions in these materials.

TABLE IIIa

Oxide	Copper–oxygen bond lengths (Å) and bond angles (°)		
	This work	Literature (from X-ray study)	Ref.
$SrCuO_2$			
Cu–O1	1 × 1.907(3)	1 × 1.89	(14)
Cu–O1	2 × 1.959(3)	2 × 1.96	
Cu–O2	1 × 1.933(3)	1 × 1.90	
O2–Cu–O1	2 × 92.3(1)		
O1–Cu–O1	2 × 87.7(1)		
Sr_2CuO_3			
Cu–O1	2 × 1.967(1)	2 × 1.96	(16)
Cu–O2	2 × 1.958(1)	2 × 1.96	
O–Cu–O	4 × 90.0		
Ca_2CuO_3			
Cu–O1	2 × 1.960(3)	2 × 1.96	(14)
Cu–O2	2 × 1.884(1)	2 × 1.89	
O–Cu–O	4 × 90.0		
Li_2CuO_2			
Cu–O	4 × 1.955(3)	4 × 1.96	(19)
O–Cu–O	2 × 93.9(2)		
O–Cu–O	2 × 86.1(2)		
Bi_2CuO_4			
Cu–O	4 × 1.937(3)	4 × 2.04	(17)
O–Cu–O	4 × 89.9(2)		
O–Cu–O	2 × 175.6(2)		
$KCuO_2$			
Cu–O	2 × 1.815(8)	2 × 1.84	(5)
Cu–O	2 × 1.832(8)	2 × 1.84	
O–Cu–O	2 × 95.3(4)		
O–Cu–O	2 × 96.5(4)		
O–Cu–O	2 × 179.4(8)		

TABLE IIIb

| | Copper–oxygen bond lengths (Å) and bond angles (°) | | |
Oxide	This work	Literature (from X-ray study)	Ref.
BaCuO$_{2.00}$			(8)
Cu1–O2	2 × 1.956(3)	2 × 1.95	
Cu1–O3	2 × 1.970(3)	2 × 1.95	
O3–Cu1–O2	2 × 84.4(3)		
O3–Cu1–O2	2 × 96.1(3)		
O3–Cu1–O3	1 × 165.0(6)		
O2–Cu1–O2	1 × 183.5(6)		
Cu2–O1	4 × 1.984(3)	4 × 1.98	
O1–Cu2–O1	2 × 86.1(3)		
O1–Cu2–O1	2 × 93.5(3)		
O1–Cu2–O1	2 × 173.4(6)		
Cu3–O1	4 × 1.941(1)	4 × 1.90	
Cu3–O5	1 × 2.407(3)	1 × 2.41	
O5–Cu3–O1	4 × 99.3(2)		
O1–Cu3–O1	4 × 88.5(2)		
O1–Cu3–O1	2 × 161.4(4)		
Cu4–O5	1 × 1.796(1)	1 × 1.80	
Cu4–O6	2 × 1.95 (1)	2 × 2.05	
O5–Cu4–O6	2 × 99.0(4)		
O6–Cu4–O6	1 × 162.1(8)		
BaCuO$_{2.07}$			(8)
Cu1–O2	2 × 1.937(3)	2 × 1.95[a]	
Cu1–O3	2 × 1.955(3)	2 × 1.95[a]	
O3–Cu1–O2	2 × 83.4(3)		
O3–Cu1–O2	2 × 96.8(3)		
O3–Cu1–O3	1 × 165.5(6)		
O2–Cu1–O2	1 × 184.5(6)		
Cu2–O1	4 × 1.999(3)	4 × 1.98[a]	
O1–Cu2–O1	2 × 86.3(3)		
O1–Cu2–O1	2 × 92.8(3)		
O1–Cu2–O1	2 × 170.4(6)		
Cu3–O1	4 × 1.948(1)	4 × 1.90[a]	
Cu3–O5	1 × 2.441(3)	1 × 2.41[a]	
O5–Cu3–O1	4 × 96.8(2)		
O1–Cu3–O1	4 × 89.2(2)		
O1–Cu3–O1	2 × 166.3(4)		
Cu4–O5	1 × 1.928(1)	—	
Cu4–O6	3.2 × 2.13 (2)	—	
O5–Cu4–O6	3.2 × 95.8(4)	—	
O6–Cu4–O6	1.6 × 162.1(8)	—	
O6–Cu4–O6	3.2 × 89.4(8)	—	

[a] Values quoted for BaCuO$_{2.00}$ single crystal.

The bond valence theory relates the oxidation state (V) of a metal to bond lengths in an analytical expression of the type

$$V = \Sigma(R_o/R_{ij})^N,$$

where R_{ij} are the various bond lengths in the coordination environment around the metal and R_o and N are empirical parameters. For copper(II), values for R_o and N have been taken from Brown and Wu (21) as 1.718 and 6, respectively. This expression was used to calculate the formal oxidation state for copper in the materials studied in this work, resulting in a series of values that ranged between 1.80 and 2.06. This illustrates how these calculated values may only be used relatively, especially when applied to high T_c superconductors, and should not be used for absolute quantitative determination of single-site valences. The empirical values taken from Brown and Wu (21) were determined for a range of materials containing copper–oxygen bonds, not only oxides. Attempts to improve the fit of our data to an oxidation level of two for copper by varying R_o and N produced minor changes. A slightly better fit was obtained for a fixed value of N ($= 6$) with $R_o = 1.735$. The effective valences obtained using this value ranged from 1.91 to 2.18 (excluding KCuO$_2$) and are summarized in Table IVa. For reference, the respective valences for the other metal centers in the compounds studied are included in this table. These have been calculated using parameters taken from Brown and Wu (21).

TABLE IVa

Oxide	V for copper ($= \Sigma(R_o/R_{ij})^N$)	V for other metal present
SrCuO$_2$	2.06(2)	1.81(2)
Sr$_2$CuO$_3$	1.91(1)	1.85(1)
Ca$_2$CuO$_3$	2.18(1)	1.83(1)
Li$_2$CuO$_2$	1.95(2)	1.05(1)
Bi$_2$CuO$_4$	2.07(2)	2.84(2)
KCuO$_2$	3.22(10)[a] 2.97 (8)[b]	1.09(2)

[a] Value obtained using the parameters relevant to Cu^{3+} given by David et al. (3) ($R_o = 1.771$ Å, $N = 7.5$).
[b] Value obtained using the parameters relevant to Cu^{2+}.

TABLE IVb

Oxide	V for copper $(= \Sigma(R_o/R_{ij})^N)$	V for barium
BaCuO$_{2.00}$		
Cu–1	1.91(2)	Ba–1 1.95(2)
Cu–2	1.79(2)	Ba–2 1.39(2)
Cu–3	2.18(1)	Ba–3 1.91(1)
Cu–4	1.82(3)	
BaCuO$_{2.07}$		
Cu–1	2.01(2)	Ba–1 2.08(4)
Cu–2	1.71(2)	Ba–2 1.57(3)
Cu–3	2.13(1)	Ba–3 1.98(1)
Cu–4	1.46(5)	

Bond valence calculations were also performed for BaCuO$_{2+x}$. The values of the formal oxidation state obtained can be seen in Table IVb. Similarly for reference, the calculated values of the site valence for barium are included in this table. Such calculations should, however, be treated with due caution as atom positions represent only the average cell contents. Hence the perceived coordination environment of Cu(4) in BaCuO$_{2.07}$ will probably be an average of copper bound to 3, 4, and 5 oxygens and the determined copper oxygen distance an average over these various geometries. This is reflected in a low calculated copper oxidation state for the site. The value for Cu(3) is somewhat high, probably reflecting a high formal oxidation state for the site when the neighboring O(5) site is adjacent to a vacant Cu(4) site.

For KCuO$_2$, where copper is present in the trivalent state, the use of values of R_o and N relevant to Cu^{3+} given by David et al. (3) or of those used for Cu^{2+} result in calculated values of the oxidation state that are close to 3. The value obtained using the parameters relevant for Cu^{2+} is quite accurate (2.97) while that obtained using David's parameters is slightly high (3.22). This slight anomaly is probably the result of a lack of precise structural information for

complex oxides containing Cu^{3+} in square planar or square pyramidal sites. Further neutron diffraction studies of such materials are planned and this data should allow the proportioning of copper oxidation states between sites in high-temperature superconductors on a more definitive basis.

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