JOURNAL OF SOLID STATE CHEMISTRY **90**, 17–26 (1991)

The Crystal Structure of $BaCuO_2$

E. F. PAULUS

Angewandte Physik, Hoechst AG, 6000 Frankfurt/Main, West Germany

AND G. MIEHE, H. FUESS, I. YEHIA AND U. LÖCHNER

Strukturforschung, Fachbereich Materialwissenschaft, Petersenstr. 20, Technische Hochschule 6100 Darmstadt, West Germany

Received March 19, 1990; in revised form July 12, 1990

The crystal structure of $BaCuO_2$ has been redetermined by single crystal X-ray study on a crystal obtained as a parasitic phase during preparation of $YBa_2Cu_3O_7$. The formula is $Ba_{0.92}Cu_{1.06}O_{2.28}$ with $a = 18.347(2)$ Å in the cubic space group $Im3m$. Reflections numbering 10,288 were collected and the structure was refined to $R_w = 0.031$ on the basis of 496 unique reflections. The structure is composed of an ordered and a disordered part of copper–oxygen units. The results for the ordered part confirm earlier structure determinations. The disorder is discussed in detail.

Introduction

Barium cuprate $BaCuO_2$ is frequently observed in the process of preparation of $YBa_2Cu_3O_{7-x}$ by flux methods as a parasitic phase. The material is nonstoichiometric; large deviations of the ideal composition are observed. The oxygen content particularly can vary. Compositions between 1.79 and 2.5 oxygen in the formula unit were reported in connection with a variation of the cell constants in crystalline powders (*1–3*). Similar observations are described for high temperature superconductors, which often contain the elements barium, copper, and oxygen.

The structure of $BaCuO_2$ was determined by Kipka and Müller-Buschbaum in 1977 by a single crystal structure analysis (*4, 6*). They found in a cubic cell of space group $Im3m$ and with $a = 18.27$ Å four different equivalent positions for barium, four for copper, and six for oxygen. Some of the positions, one oxygen and one copper position, were not fully occupied. One of the difficulties of the structure, however, is the location of a Ba atom in the origin, because the nearest neighbors are not oxygens, but 12 Cu atoms (3.24 Å). Another six Cu atoms have distances of 3.76 Å and 24 O atoms have distances of 3.87 Å. Another point is the location of atom O(4). It is only coordinated to Ba(2) (3.24 Å), but not to any Cu atoms. Cu(4) and O(6) are partly occupied.

In a powder neutron diffraction study (*5*) the basic results of Kipka and Müller-Buschbaum were confirmed. No atom was located at the origin, what was also suggested by Müller-Buschbaum recently (*6*). The refinement on two samples, namely $BaCuO_{2.00}$ and $BaCuO_{2.07}$, placed the excess oxygen into the partially occupied oxygen

0022-4596/91 $3.00

TABLE I

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT COEFFICIENTS (Å^2)

	X	Y	Z	U(eq)	Occup.
Ba(1)	0	6870(1)	1520(1)	0.022(1)	1
Ba(2)	3619(1)	3619(1)	0	0.023(1)	1
Ba(3)	1769(1)	1769(1)	1769(1)	0.010(1)	1
Cu(1)	−3509(1)	2500	1491(1)	0.013(1)	1
Cu(2)	1247(1)	0	1247(1)	0.008(1)	1
Cu(3)	7950(2)	0	0	0.008(1)	1
Cu(4)	0	5665(4)	0	0.079(3)	0.89(2)
Cu(5)	2500	5000	0	0.054(4)	0.59(2)
O(1)	743(4)	8136(6)	743(4)	0.014(3)	1
O(2)	6465(4)	6465(4)	−1616(7)	0.020(3)	1
O(3)	4140(7)	2323(4)	2323(4)	0.018(3)	1
A(1)	0	10000	0	0.04 (3)	0.54(4)
A(2)	0	6471	1687	0.03 (2)	0.29(2)
A(3)	446	8963	0	1.0 (6)	0.20(1)
A(4)	0	3347(14)	0	0.027(7)	1
A(5)	0	5000	0	0.03 (2)	0.52(3)
A(6)	740	5000	0	0.04 (2)	0.35(2)
A(7)	0	6346	0	0.3 (2)	0.28(2)
A(8)	1312	4498	0	0.07 (2)	0.23(2)
A(9)	676(14)	−4324(14)	2500	0.03 (1)	0.35(4)
A(10)	875	5000	2824	0.09 (4)	0.20(1)

Note. A-positions are partly filled and/or disordered. Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

position O(6) with occupancies of 0.25 and 0.379, respectively.

Preliminary results of our investigations were given earlier (*7*).

Experimental

The crystal was obtained as a parasitic phase during the preparation of $YBa_2Cu_3O_{7-x}$ from flux. A cubelike regulus, the preparation of which is described elsewhere (*8*), was kindly given to us by Dr. W. Assmus (University Frankfurt/Main). The regulus was carefully crashed into a few splinters. One of these proved to be a single crystal of $YBa_2Cu_3O_{7-x}$, which was examined by X-ray diffraction. The results revealed that this particular specimen is a real single crystal phase (*8, 9*). Another splinter was a cube of dimensions 0.1 × 0.1 × 0.05 mm, the crystal examined here. EDX-measurements showed the presence of Ba and Cu, but no other metals. The crystal was sealed into a Lindemann-glass capillary.

Twenty-five reflections were used for the cell refinement: a = 18.347 (2) Å, $Im3m$, $V = 6175.8\,(12)$ Å^3, $Z = 96$, $Ba_{0.92}Cu_{1.06}O_{2.28}$, M = 232.1, D = 5.991 g/cm^3, $F(000)$ = 9743.7. The experimental conditions for the cell determination and the X-ray intensity measurements were: $\lambda(\mathrm{Mo}K\alpha)$ = 0.7107 Å, graphite monochromator, μ = 22.47 mm^{-1}, T = 293 K, computer controlled Nicolet R3 diffractometer, $2\vartheta/\vartheta$-scan, 4 to 20° min^{-1}, $2\vartheta_{\max}$ = 47°, one standard reflection. The 10,288 measured reflections (h, k, l: −20 to +20) resulted in 496 unique reflections (R_{int} = 4.9%), which were all bigger than $1\sigma(F)$. Semiempirical absorption correction ac-

TABLE II

SELECTED ATOMIC DISTANCES

Atoms	Distance	Frequency	Atoms	Distance	Frequency
Ba(1)–Cu(1)	3.347(8)	2x	–Cu(2)	3.490(8)	1x
–Cu(3)	3.420(8)	1x	–Cu(4)	3.559(8)	1x
–Cu(5)	3.875(8)	1x	–O(1)	3.046(10)	2x
–O(2)	2.729(10)	2x	–O(3)	2.773(10)	2x
–A(2)	0.795(10)	1x	–A(4)	2.816(10)	1x
–A(7)	2.949(10)	1x	–A(8)	2.539(10)	1x
–A(9)	3.095(10)	2x	–A(10)	2.188(10)	1x
Ba(2)–Cu(1)	3.426(8)	4x	–Cu(4)	3.781(8)	2x
–Cu(5)	3.261(8)	2x	–O(2)	2.972(10)	2x
–O(3)	2.909(12)	2x	–A(6)	2.792(10)	2x
–A(8)	2.698(10)	4x	–A(9)	2.725(10)	4x
–A(10)	2.806(10)	6x			
Ba(3)–Cu(1)	3.501(8)	6x	–Cu(2)	3.517(8)	3x
–O(1)	2.668(11)	3x	–O(2)	3.067(10)	3x
–O(3)	2.888(12)	3x			
Cu(1)–O(2)	1.914(8)	2x	–O(3)	1.943(9)	2x
–A(9)	2.114(9)	1x			
Cu(2)–O(1)	1.999(6)	4x	–A(3)	1.520(9)	2x
–A(3)	2.460(9)	4x			
Cu(3)–O(1)	1.958(11)	4x	–A(3)	2.031(9)	4x
–A(4)	2.379(9)	1x			
Cu(4)–A(4)	1.813(9)	1x	–A(5)	1.219(9)	1x
–A(6)	1.825(9)	4x	–A(7)	1.250(9)	1x
–A(8)	2.426(9)	4x			
Cu(5)–A(8)	2.366(9)	4x	–A(9)	1.754(9)	4x
–A(10)	1.712(9)	4x			
O(1) –Ba(1)	3.046(10)	2x	–Ba(3)	2.668(11)	1x
–Cu(2)	1.999(6)	2x	–Cu(3)	1.958(11)	1x
O(2) –Ba(1)	2.729(10)	2x	–Ba(2)	2.972(10)	1x
–Ba(3)	3.067(10)	2x	–Cu(1)	1.914(8)	2x
O(3) –Ba(1)	2.773(10)	2x	–Ba(2)	2.909(12)	1x
–Ba(3)	2.888(12)	1x	–Cu(1)	1.943(9)	2x
A(1) –Cu(2)	3.236(12)	12x	–Cu(3)	3.762(12)	6x
–O(1)	3.925(12)	24x			
A(4) –Ba(1)	2.816(10)	4x	–Cu(3)	2.379(9)	1x
–Cu(4)	1.813(9)	1x			
A(8) –Ba(1)	2.539(10)	1x	–Ba(2)	2.698(8)	2x
–Cu(4)	2.426(9)	1x	–Cu(5)	2.366(9)	1x
–A(8)	1.842(10)	1x			
A(9) –Ba(1)	3.095(10)	2x	–Ba(2)	2.725(10)	2x
–Cu(1)	2.114(9)	1x	–Cu(5)	1.754(9)	1x

cording to the ψ-method (*10*) was performed, but not extinction correction was possible. Instead of that 8 larger reflections had to be left out, because they were severely affected by extinction, as was shown later on in the analysis. The solution of the phase problem was obtained by direct methods (*10*). The coordinates of the ordered part of the structure could be found immediately [Ba(1), Ba(2), Ba(3), Cu(1), Cu(2), Cu(3), O(1), O(2), O(3), *A*(4)]. After a couple of least squares cycles [minimized quantity: $\Sigma w(F_0 - F_c)^2$, where w is chosen according to the counting statistics] we got a weighted *R*-value of 0.145. After a few difference Fourier syntheses and further refinement the presence of additional partially occupied Cu positions with surrounding oxygens was confirmed. The latter ones are in Tables I and II given as "*A*," to point out that there is a certain probability that a part of these electron density maxima can also be interpreted as partially occupied O and/or Cu positions. These *A* atoms are connecting the almost fully ordered parts of the structure, they are in a way separated from the former ones. All the *A* atoms were given the scattering factor of O. The relative multiplicity factors and the coordinates of these *A* atoms were determined in a difference Fourier synthesis, when all these electron density maxima were not yet in the atom list. Only the common multiplicity factor and the isotropic temperature coefficients of these atoms were refined by least squares.

It was possible to refine a reasonable temperature coefficient for *A*(1), the atom in the origin. Omitting this atom in the refinement caused a relatively large maximum in the difference Fourier synthesis, whereas putting it in swept this maximum away.

The 10 largest maxima in the last difference Fourier synthesis of the electron density are between 1.6 and 2.6 electrons/Å^3. The biggest change of a parameter in the last cycle of the least squares refinement was smaller than 7% of its standard deviation. The goodness of fit is 5.3. The weighted *R*-value[1] is 0.031, the unweighted one 0.057. The atomic coordinates together with the equivalent isotropic displacement coefficients and the occupancies are given in Table I; selected atomic distances together with their frequencies in Table II.

All calculations were performed with the SHELXTL (*10*) and SHELXTL-PLUS programs (*11*). Atomic scattering factors were taken from "International Tables for X-ray Crystallography" (*12*).

Discussion

The ordered part of the structure is almost the same as that determined by the group of Müller-Buschbaum (*4, 6*). The cell constant *a* has changed from 18.27 to 18.347 Å. Kipka and Müller-Buschbaum gave for their sample the stoichiometric formula $BaCuO_2$, whereas we have found the formula $Ba_{0.92}Cu_{1.06}O_{2.28}$. There are serious differences between the two samples. According to (*1–3*) the cell constant *a* is increasing with the oxygen content. Weller and Lines (*5*) are assuming that the surplus oxygen is filling up the *A*(8)-position [they called it O(6)]. Our results are not in agreement with that; there are 7 or 8 atomic positions [*A*(1), *A*(5), *A*(6), *A*(7), *A*(8), *A*(9), *A*(10) and possibly *A*(3)], which can be filled up with oxygen.

Furthermore, we have found instead of O(4) (*4, 5*) a new Cu(5) position, which has, in a similar manner to Cu(4), partly filled O surroundings. There is an atomic position *A*(1) in 0,0,0, that Weller and Lines (*5*) and Kipka and Müller-Buschbaum (*4, 6*) denied. This position must be an O and not a Cu site. The nearest neighbors are Cu(2) (3.236 Å) and Cu(3) (3.762 Å). The distance of O(1) is definitely much longer (3.925 Å). In the

---

[1] Tables for anisotropic thermal displacement coefficients, for angles (bond angles), and distances (bond lengths) in atomic configurations and for structure factors are deposited. NAPS document No. 04820 for 16 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10613. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for each additional 10 pages of material, $1.50 for postage of any microfiche orders.

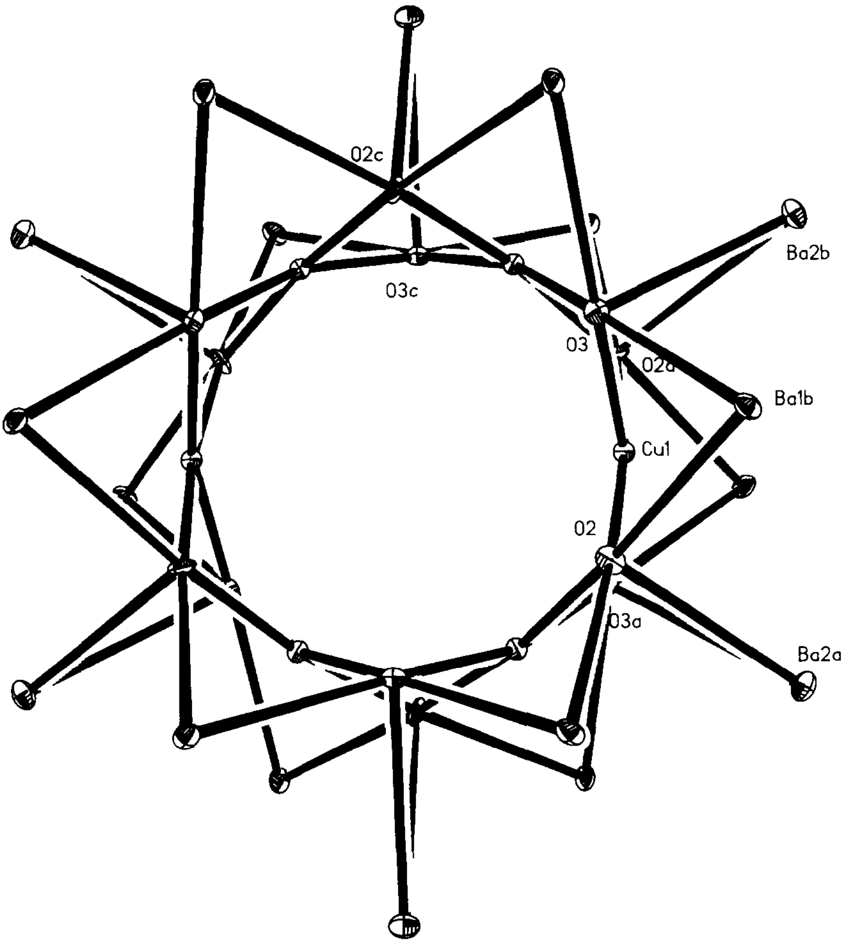

FIG. 1. The planar twice-oxygen-bridged six-membered Cu ring Cu_6O_{12} together with Ba(1) and Ba(2).

first sphere there are 12, in the second 6, and in the third 24 neighbors. The site in 0, 0, 0 is about half filled.

The configurations of other atoms are given in Table II. The oxygens O(1), O(2), and O(3) and the atoms $A(4)$, $A(8)$, and $A(9)$, which are at least to a certain amount oxygens, have a distorted octahedral configuration of Ba and Cu atoms. All five Cu atoms show a square planar or distorted square planar configuration. In addition to that Cu(1) has $A(9)$ (2.114 Å) as the apex atom for a square pyramid and Cu(3) has $A(4)$ (2.379 Å). The apex atom for Cu(4) is also $A(4)$ (1.813 Å). For Cu(2) and Cu(5) the situation is much more complex. The center of gravity of 6 symmetry equivalent positions of $A(3)$ is at the apex of a tetragonal pyramid around Cu(2); the centers of gravity of two symmetry equivalent $A(8)$ positions are at the apices of tetragonal bipyramides around Cu(5). All the Cu atoms have therefore a "perowskit like" configuration.

Figures 1 and 2 show the two fully ordered clusters of the structure together with the Ba atoms. The satellite peaks of Ba(1) (0.795 Å) and Cu(2) (1.520 Å) are not shown. Especially in the case of Cu(2) it cannot be ex-

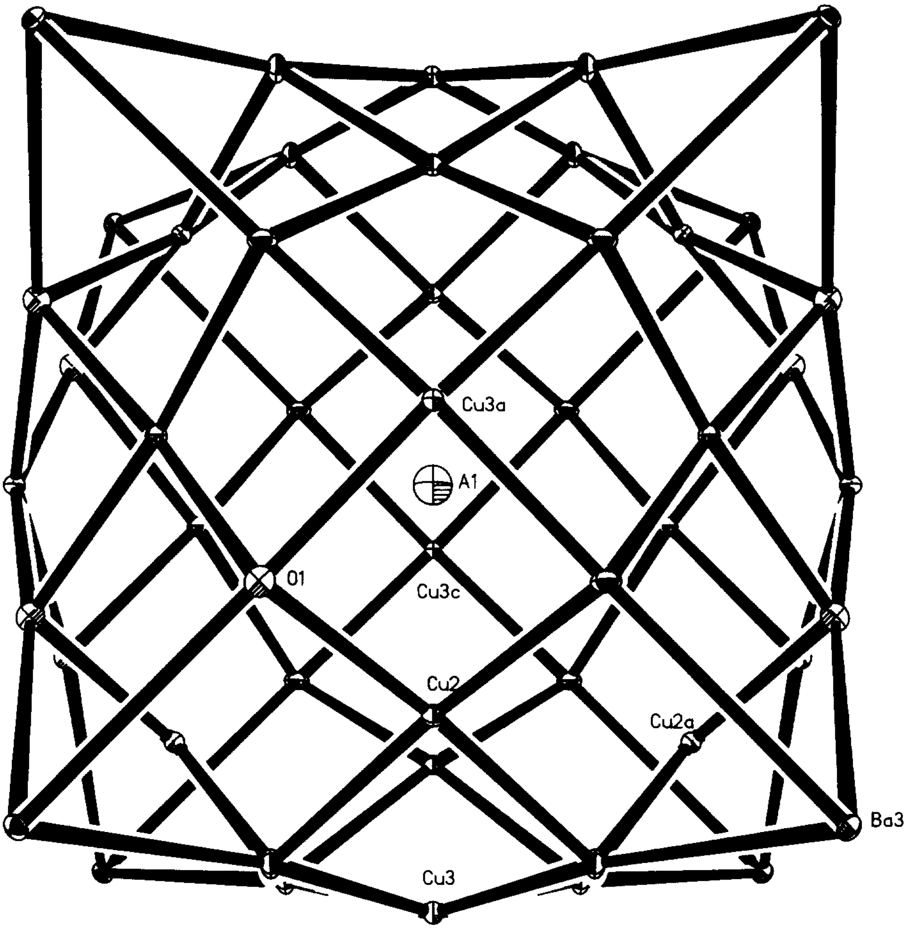

FIG. 2. The twenty-six-faced cluster $Cu_{18}O_{24}$ together with A(1) and Ba(3).

cluded that the satellite is in reality, to a certain amount, filled with oxygen. These two main clusters are controlling the architecture of the structure. One of them is a Cu_6O_{12} ring and centers at 8*c* (1/4,1/4,1/4) (Fig. 1). The other one is a $Cu_{18}O_{24}$ group, which involves Cu(2), Cu(3), and O(1) in a spherical cage (Fig. 2). O(1) occupies the corners of a polyhedron with point symmetry *m*3*m*. This cage consists of six squares centered by Cu(3) [parallel (100)], 12 rectangular faces centered by Cu(2) [parallel (110)] and eight empty regular triangles [parallel *(111)]*. The oxygens of the last ones are also coordinating Ba(3). The Cu atoms are slightly out of plane: Cu(2) is 0.141 Å shifted toward the center of the polyhedron; Cu(3) is 0.344 Å pushed outward. The O(1)–O(1) distances forming common edges of CuO_4 groups [2.718 Å] are shorter than O(1)–O(1) distances connecting the corners of the empty triangles [2.909 Å]. The polyhedron would be an archimedic one for $x(O(1))/(1-y(O(1))) = 1/(\sqrt{2}+1) = 0.4142$; actually it is 0.3986. The planar six-membered Cu ring in the Cu_6O_{12} group is formed by Cu(1). Each side of the six-membered ring is bridged by O(2) and O(3). Again the com-

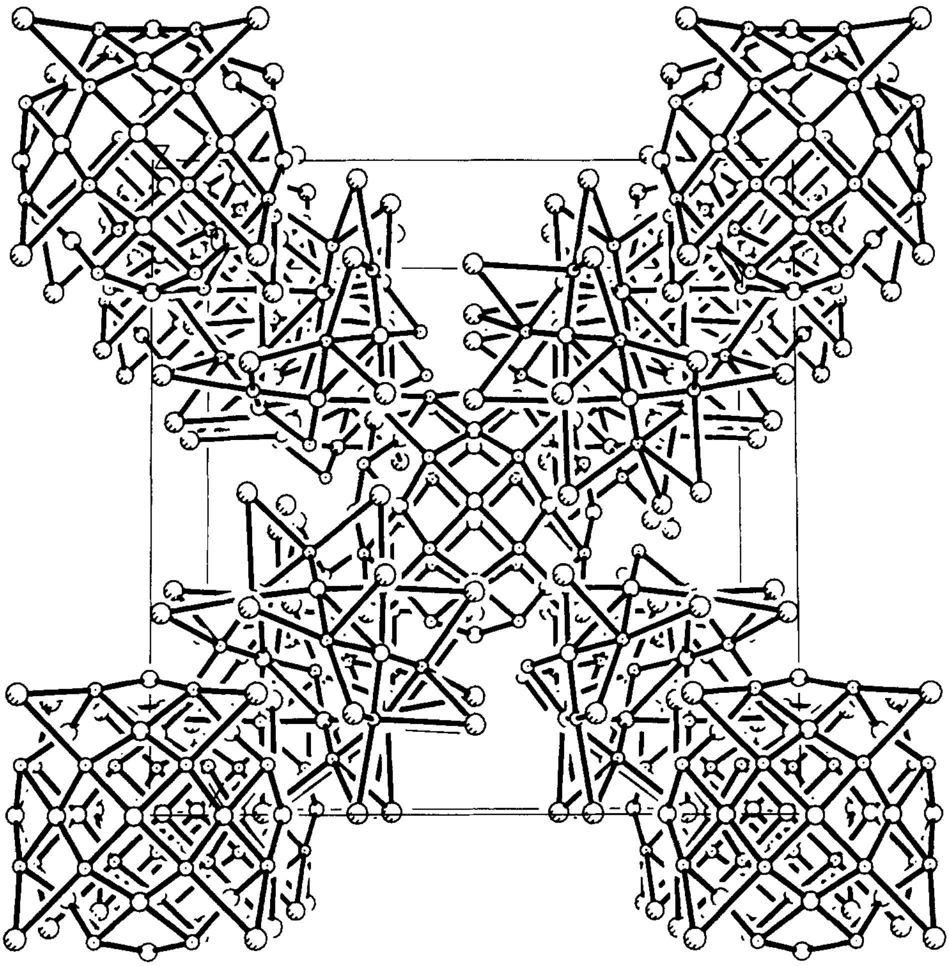

FIG. 3. The ordered part of the copper–oxygen structure together with the Ba atoms.

mon edges of the CuO_4 rectangles are significantly shorter (2.618 Å) than the unshared ones (2.804 Å). The angle between the planes of a rectangle and the six-membered ring is 90° and that between the rectangles themselves is 60°. Ba(1) atoms are bridging O(2) and O(3) atoms in the plane of the ring, Ba(2) atoms are bridging perpendicular to the plane.

These two ordered clusters are arranged along the main diagonals [111] of the cell (Fig. 3). Ba(3) atoms are connecting the two atomic groups. Ba(1) and Ba(2) are sitting on the periphery of the six-membered ring in such a manner that this cluster is enveloped by positively charged Ba ions. Along the cell edges, and parallel to these for the cages in 1/2, 1/2, 1/2, however, Cu(3) is coordinated by $A(4)$ (2.379 Å), which generates the connection to the disordered part of the structure. The ordered part [$A(4)$ included] gives the formula $Ba_{0.92}Cu_{0.875}O_{1.625}$, what means, that there is a deficiency of oxygen, which has to be compensated.

The disordered part consists of another two clusters without any further Ba atom. The partly filled Cu(4) position, being 0.229 Å out of the plane built by four equivalent

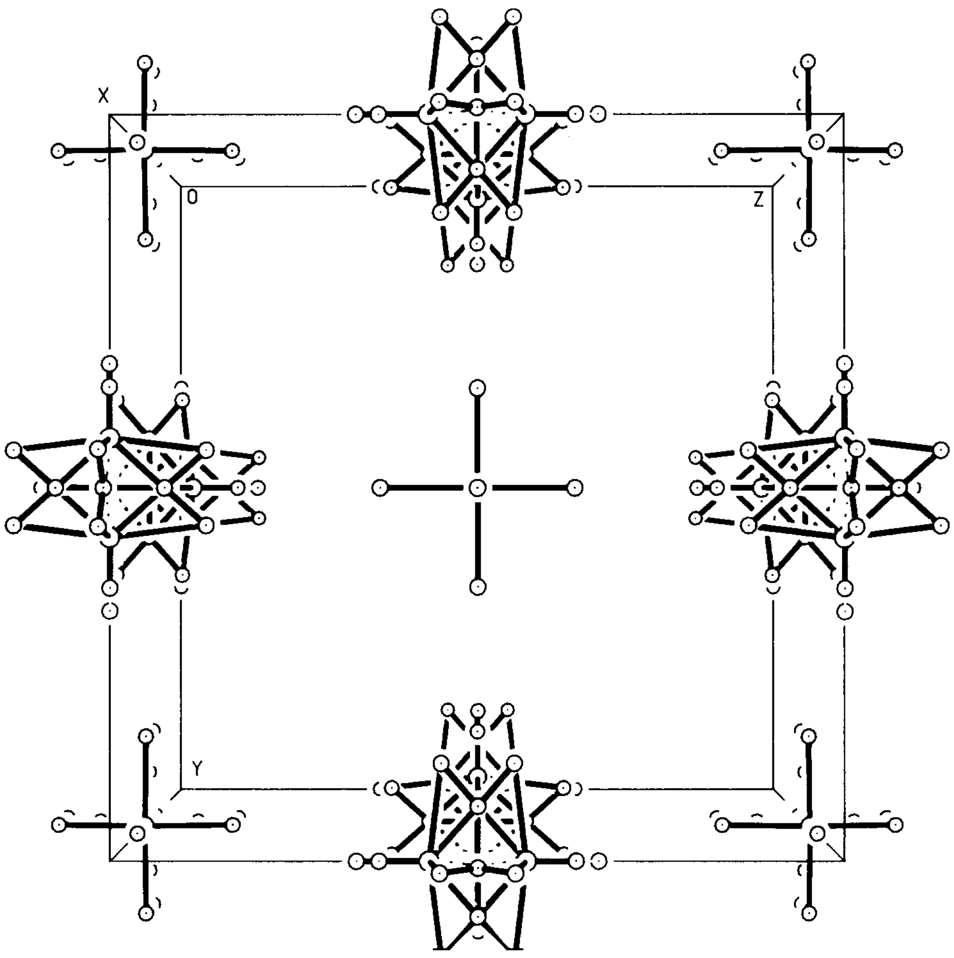

FIG. 4. The Cu(4)O clusters in the crystal cell.

sites of A(8) (2.426 Å), is also coordinated by A(4) (1.813 Å). The plane of symmetry in $x = 0.5$ generates another Cu(4)O_4 group with a Cu–Cu distance of 2.434 Å, resulting in a "twinned" group, shown in Fig. 4. In the plane of symmetry, however, rather high electron density maxima are located, which together with *A*(7) suggest that we have a real mass of disordering of O and Cu. This might be the reason for the distance of 1.842 Å between two *A*(8) atoms being too short. Cu(5) together with its coordination sphere shows a still larger amount of disordering (Fig. 5). The main coordination is the planar one by *A*(9) (1.754 Å). *A*(10) (1.712 Å) has the disordered positions for the planar coordination and *A*(8) [2.366 Å] generates common edges with the coordination sphere of Cu(4).

The Cu(4)O clusters are interconnecting the ordered cages via the faces parallel (100) and via *A*(4) atoms, which coordinate both groups. The connections are centered along the cell edges for the cages in the origin, and parallel to these shifted by 1/2,1/2,1/2 (I-centered cell) for the cages in the center of the cell. The Cu(5)O clusters join by common *A*(8)–*A*(8) edges the Cu(4)O clusters

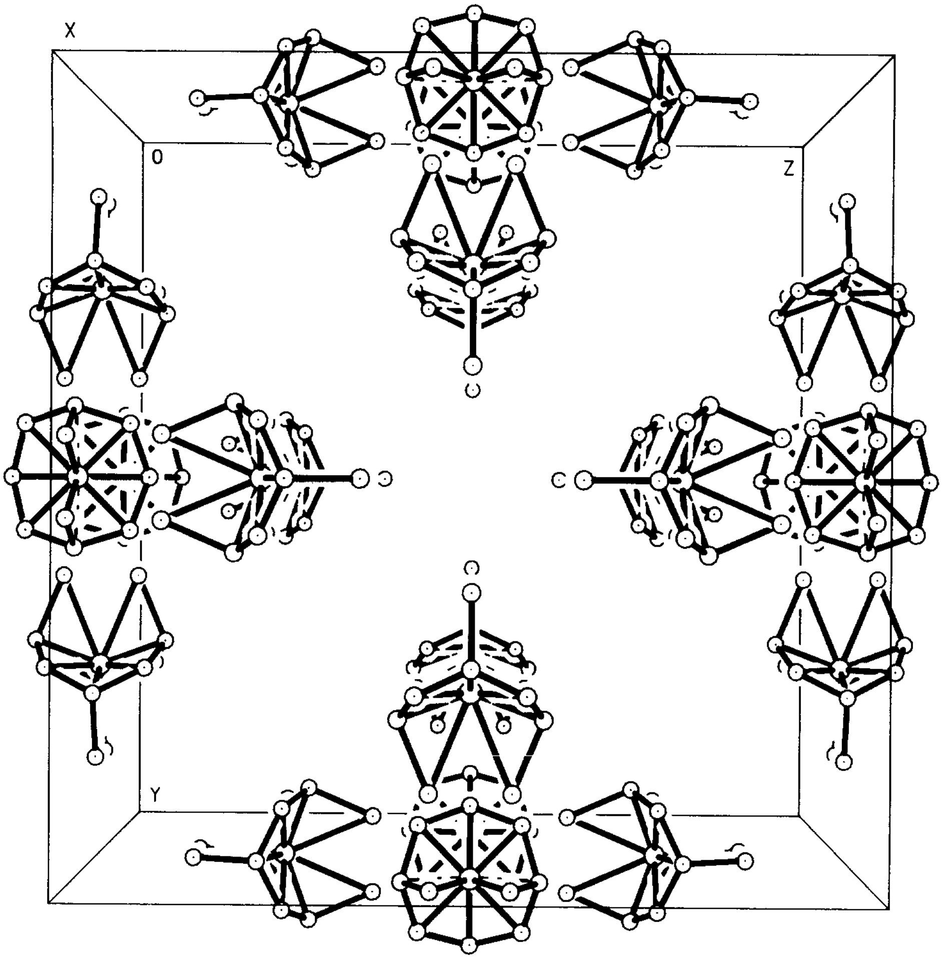

FIG. 5. The Cu(5)O clusters in the crystal cell.

connecting the cages in the origin of the cells and the Cu(4)O clusters connecting the cages in the center of the cells. Like strings around a parcel, chains of atomic groups, Cu(4)O clusters alternating with Cu(5)O clusters, are reeled around the cell. These chains or strings are wrapped in Ba ions. This means that channels parallel to the cell edges are running through the crystal and these channels are coated with Ba ions. In this way there is a partition between the ordered and the disordered parts of the structure. Having this model in mind one can imagine that such a degree of disordering is possible and that our sample is nonstoichiometric. Figure 4 shows the distribution of the Cu(4)O clusters and Fig. 5 the distribution of the Cu(5)O clusters in the cell.

The sample investigated by Kipka and Müller-Buschbaum (*4*, *6*) was obtained by melting the oxides, whereas our sample was obtained as a parasitic crystal phase synthesizing $YBa_2Cu_3O_{7-x}$ by the flux method. This seems to create the observed dramatic differences. We have also synthesized Ba-

CuO_2 by melting the oxides and we have grown crystals from that sample. High resolution synchrotron powder patterns revealed the presence of broad diffuse lines, which might be due to the disorder system. Measurements on single crystals will be compared with the results of powder measurements. Furthermore we are doing measurements at low temperature on the above-investigated crystal. Perhaps then we will be able to solve a few more of the raised questions.

Acknowledgments

We thank Dr. W. Assmus (University Frankfurt/Main) for the crystal. This work was supported by the Bundesminister für Forschung und Technologie (Bonn) Grant 03-FU1FRA.

References

1. S. Eriksson, L-G. Johansson, L. Boerjesson and M. Kakihana, *Physica C* **59,** 162 (1989).
2. M. Kakihana, L. Boerjesson, and S. Eriksson, private communication (1989).
3. M. Arjomand and D. J. Machin, *J. Chem. Soc.*, Dalton Trans., 1061 (1975).
4. R. Kipka and H. K. Müller-Buschbaum, *Z. Naturforsch.* **32b,** 121 (1977).
5. M. T. Weller and D. R. Lines, *J. Chem. Soc. Chem. Commun.*, 484 (1989).
6. W. Gutau and H. K. Müller-Buschbaum, *J. Less-Common Met.* **152,** L11 (1989).
7. E. F. Paulus, J. Bock, H. Fuess, and I. Yehia. *Z. Kristallogr.* **186,** 225 (1989).
8. K. Brodt, H. Fuess, E. F. Paulus, W. Assmus, and J. Kowalewski, *Acta Crystallogr.* **C46,** 354 (1990).
9. E. F. Paulus, K. Brodt, H. Fuess, W. Assmus, and J. Kowalewski, *Z. Krist.* **185,** A4 (1988).
10. G. M. Sheldrick, SHELXTL, an Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Universität Göttingen (1983).
11. G. M. Sheldrick, SHELXTL-PLUS, an Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Universität Göttingen (1988).
12. International Tables for X-ray Crystallography, Vol. IV, pp. 55, 99, 149. Kynoch Press, Birmingham (1974).