

## Neutron study of the crystal structure and vacancy distribution in the superconductor $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$

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Two samples of the high-temperature superconductor  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$  with  $\delta=2.0$  and  $2.2$  have been studied at room temperature and at 10 K, with the neutron powder diffraction method and profile analysis. The structure of the compound is orthorhombic. The oxygen atoms are located on four sets of sites and not on five sets as reported earlier in x-ray-diffraction studies. Of the two sets of copper atoms, one is surrounded by four oxygen atoms at distances 1.9299(4) and 1.9607(4) Å. This arrangement forms a two-dimensional framework of Cu-O atoms that extends indefinitely along the  $a$  and  $b$  axis. A fifth oxygen atom is located at 2.295(3) Å from the copper atom, giving a pyramidal configuration. In the other set, the Cu atoms are also surrounded by four oxygen atoms, with distances 1.9429(1) and 1.846(2) Å. In this case, however, the oxygen atoms form rectangles connected by vertices, and resulting in chains along the  $b$  axis. In the compound with  $\delta=2.0$  all oxygen sites are fully occupied. When  $\delta=2.2$  there are oxygen vacancies, but these are confined to one set of positions only, specifically to the oxygen atoms of the chains, located on the  $b$  axis. No detectable change of the structure has been observed between room temperature and low temperature.

The discovery of superconductors with values of the critical temperature of the order of 90–95 K in the Y-Ba-Cu-O system has stimulated intense research work aimed at the identification and characterization of the materials with high values of  $T_c$ .

It has been found in a number of investigations<sup>1,2</sup> that the superconducting phase has the composition  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$  (with  $\delta \approx 2$ ) and that the structure of the compound can be described as a distorted oxygen-deficient perovskite.<sup>1</sup> Structural investigations of  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$  have been carried out using single-crystal<sup>2-4</sup> and powder<sup>5</sup> x-ray-diffraction techniques. The structure of the compound has been refined in space groups  $Pmmm$ ,<sup>3</sup>  $P4/mmm$ ,<sup>2</sup> and  $P4m2$  (Ref. 4) with no significant differences in the assignment of the metal atoms. The crystallographic features of the oxygen atoms, however, are quite different in the three space groups. Adopting the nomenclature of Ref. 3 (which has been followed throughout this paper), we have a situation where atoms O(2) and O(3) are crystallographically equivalent in space group  $P4/mmm$  but not in  $Pmmm$  and  $P4m2$ , while atoms O(4) and O(5) occupy equivalent positions in space groups  $P4/mmm$  and  $P4m2$ , but not in  $Pmmm$ , where they split into two inequivalent sets. It was reported in Refs. 2 and 3 that only half of the sites of atoms O(4) and O(5) are occupied, with the oxygen vacancies randomly distributed in the plane of the Cu(1) atoms. The x-ray powder-diffraction intensities of Beyers *et al.*<sup>5</sup> were best fitted by a model having oxygen vacancies ordered on the barium planes at  $z \approx 0.18$ , while the high-resolution transmission electron microscopy suggests that these vacancies are present on the copper planes between the barium planes.

The discrepancies between the above x-ray studies may reflect true differences in the samples prepared under different conditions in different laboratories or may result

from other causes, such as the difficulty of determining the oxygen atoms in structures in which heavy metal atoms are also present. One additional problem may arise from twinning, whose presence has been detected in single crystals of the compound.<sup>5</sup>

In this Rapid Communication, we describe a powder neutron diffraction study of  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$ . This work was undertaken not only to solve the ambiguities left by the x-ray-diffraction experiments, but also to determine with precision the oxygen atomic positions. In order to clarify the effect that different preparation procedures may have on the structure of this important material and to detect any possible changes in the structure with the temperature we have examined two samples, one which was annealed in oxygen and the other which was prepared in the same way except that it was not annealed. The compositions were synthesized from intimately mixed powders of the correct stoichiometry of basic copper carbonate (Cu content 55.8%), barium carbonate (99.5%), and yttrium oxide (99.9%). Initially the reactants were contained in platinum or gold crucibles. However, at high-temperatures ( $> 900^\circ\text{C}$ ) extensive reaction occurred between the sample and the containers. This problem was circumvented by pressing the reaction powders into pellets and stacking the pellets on top of each other. The stack then was placed on a platinum base during firing. This strategy limited the parasitic reaction to the bottom pellet which was discarded.

The samples were heat treated for 16 h at  $580^\circ\text{C}$  followed by 20 h at  $900^\circ\text{C}$  and 20 h at  $950^\circ\text{C}$ . After each heat treatment the pellets were broken up, the powder was reground and the sample that was to be annealed in oxygen was pressed into new pellets. The sample that was not to be annealed was fired in the form of free powder sitting on pellets. This sample was removed from the furnace at  $950^\circ\text{C}$  and air quenched to room temperature. Attempts

to air quench pellets rather than the powder gave nonequilibrated samples that displayed split reflections in the powder pattern.

The oxygen annealing was performed in an inert atmosphere furnace on pressed pellets of the materials at 750°C for 27 h. To ensure equilibration the sample was cooled in the furnace from 750°C to room temperature under a continuous flow of oxygen. These techniques resulted in pure single-phase materials as determined by powder x-ray-diffraction techniques. The starting lattice parameters for the refinement were obtained by performing least-squares analysis on an x-ray pattern of the material mixed with a silicon standard.

The neutron-diffraction measurements were performed on the high-resolution five-counter powder diffractometer at the National Bureau of Standards Reactor, with neutrons of wavelength 1.548 Å. The data were collected in the 2θ angular range 5°–120°, using for the in-pile monochromatic beam and diffracted beam collimators horizontal angular divergencies of 10', 20', and 10', respectively. The intensities diffracted by the two samples were measured at room temperature and at 10 K. A vanadium can of about 1 cm in diameter was used for the room-temperature measurements and an aluminum container of the same diameter for those at 10 K. The positions of the patterns containing peaks from the aluminum can were excluded from refinement. No extra peaks were observed in either sample, showing that the materials analyzed were pure one-phase compounds. The refinement was performed using the Rietveld method<sup>6</sup> adapted to the five-counter diffractometer and modified to include background parameters.<sup>7</sup> The peak profiles were in all cases described well by a Gaussian function. The neutron scattering amplitudes used were  $b(\text{Ba})=0.525$ ,  $b(\text{Y})=0.775$ ,  $b(\text{Cu})=0.772$ , and  $b(\text{O})=0.580 \times 10^{-12}$  cm. In the final refinements all structural, lattice, and profile parameters were allowed to vary simultaneously until the weighted  $R$  factor,  $R_w$ , differed by less than one part in a thousand in two successive cycles. In all cases, a difference Fourier map was calculated in order to detect if any extra nuclear density was left unaccounted for.

All refinements were carried out in space group  $Pm\bar{m}m$ . Attempts to use  $Pmm2$  did not improve the agreement factors, and the atomic coordinates were not significantly different from those obtained for  $Pm\bar{m}m$ . In addition, some thermal parameters refined to unreasonably low values. We may therefore conclude that on the basis of our data there is no evidence whatsoever that the structure is noncentrosymmetric. During refinement of the oxygen temperature factors it was immediately clear that the neutron data were consistent with a model in which the sites of atoms O(4) at  $0 \frac{1}{2} 0$  are fully (or almost fully) occupied and those of atoms O(5) at  $\frac{1}{2} 0 0$  are empty (or almost empty), and that none of the structures determined in the x-ray studies was entirely acceptable. In particular, this distribution of the oxygen atoms rules out the possibility of tetragonal symmetry for this compound. Careful analysis of the temperature and occupancy factors of the atoms O(4) and O(5) showed that the O(5) sites are completely empty. The final structural parameters are presented in Table I and the relevant bond distances are

TABLE I. Structural parameters for  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$ . (The first and second set of coordinates for each atom are for the nonannealed sample at room temperature and at 10 K, respectively. The third and fourth set are for the annealed sample at room temperature and at 10 K, respectively.) The space group is  $Pm\bar{m}m$ .

	$X$	$Y$	$Z$	$B$	$n$
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.1866(5)	0.69(6)	1.0
	$\frac{1}{2}$	$\frac{1}{2}$	0.1854(2)	0.41(6)	1.0
	$\frac{1}{2}$	$\frac{1}{2}$	0.1839(2)	0.65(5)	1.0
	$\frac{1}{2}$	$\frac{1}{2}$	0.1837(2)	0.27(6)	1.0
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.70(5)	0.5
	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.41(6)	0.5
	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.56(4)	0.5
	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.38(5)	0.5
Cu(1)	0	0	0	0.63(5)	0.5
	0	0	0	0.29(5)	0.5
	0	0	0	0.55(4)	0.5
	0	0	0	0.30(5)	0.5
Cu(2)	0	0	0.3562(3)	0.63(5)	1.0
	0	0	0.3559(1)	0.26(4)	1.0
	0	0	0.3547(1)	0.49(4)	1.0
	0	0	0.3546(1)	0.25(4)	1.0
O(1)	0	0	0.1576(3)	0.91(7)	1.0
	0	0	0.1585(2)	0.53(6)	1.0
	0	0	0.1581(2)	0.78(5)	1.0
	0	0	0.1593(2)	0.53(5)	1.0
O(2)	$\frac{1}{2}$	0	0.3790(4)	0.66(6)	1.0
	$\frac{1}{2}$	0	0.3777(2)	0.53(5)	1.0
	$\frac{1}{2}$	0	0.3779(2)	0.57(5)	1.0
	$\frac{1}{2}$	0	0.3780(2)	0.29(5)	1.0
O(3)	0	$\frac{1}{2}$	0.3774(3)	0.56(6)	1.0
	0	$\frac{1}{2}$	0.3778(2)	0.22(6)	1.0
	0	$\frac{1}{2}$	0.3776(2)	0.55(5)	1.0
	0	$\frac{1}{2}$	0.3772(2)	0.32(5)	1.0
O(4)	0	$\frac{1}{2}$	0	1.8(2)	0.397(6)
	0	$\frac{1}{2}$	0	1.3(1)	0.426(5)
	0	$\frac{1}{2}$	0	1.73(9)	0.5
	0	$\frac{1}{2}$	0	1.2(1)	0.5
	$R_N$	$R_P$	$R_w$	$R_E$	$\chi$
	4.40	7.61	10.07	7.74	1.30
	3.51	6.10	8.68	4.24	2.05
	4.84	6.10	8.40	5.42	1.55
	4.25	6.09	8.62	5.43	1.59
	$a$	$b$	$c$	$V$	
	3.8250(1)	3.8864(1)	11.6945(4)	173.85(1)	
	3.8174(1)	3.8804(1)	11.6520(3)	172.60(1)	
	3.8198(1)	3.8849(1)	11.6762(3)	173.27(1)	
	3.8126(1)	3.8804(1)	11.6333(3)	172.11(1)	

TABLE II. Bond distances in the structure of  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$ .

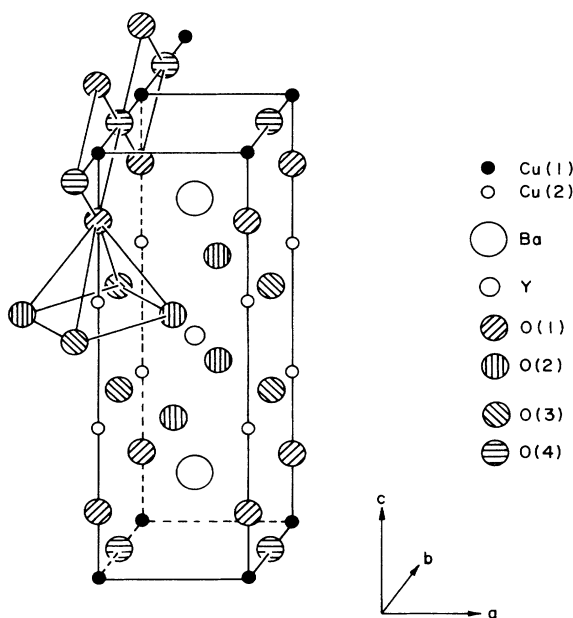
(4×)Ba-O(1) 2.7470(8)	(4×)Y-O(2) 2.403(3)	(2×)Cu(1)-O(1) 1.843(3)	(1×)Cu(2)-O(1) 2.323(4)
2.7396(4)	2.407(1)	1.847(2)	2.299(3)
2.7408(4)	2.409(1)	1.846(2)	2.295(3)
2.7346(4)	2.403(1)	1.853(2)	2.272(3)
(2×)Ba-O(2) 2.972(3)	(4×)Y-O(3) 2.389(2)	(2×)Cu(1)-O(4) 1.9428(1)	(2×)Cu(2)-O(2) 1.9305(6)
2.964(2)	2.381(1)	1.9402(1)	1.9255(4)
2.984(2)	2.386(1)	1.9429(1)	1.9299(4)
2.979(2)	2.382(1)	1.9401(1)	1.9296(4)
(2×)Ba-O(3) 2.938(6)		(2×)Cu(1)-O(5) 1.9121(1)	(2×)Cu(2)-O(3) 1.9585(8)
2.944(2)		1.9087(1)	1.9568(4)
2.960(2)		1.9099(1)	1.9607(4)
2.949(2)		1.9062(1)	1.9578(4)
(2×)Ba-O(4) 2.901(4)			
2.883(2)			
2.874(2)			
2.866(2)			
(2×)Ba-O(5) 2.922(4)			
2.904(2)			
2.896(2)			
2.886(2)			

given in Table II, and an overall view of the structure is shown in Fig. 1. From the tables it is evident that there is no detectable difference between the structures at room temperature and those at 10 K. On the other hand, the O(4) sites are fully occupied in the annealed sample and only partially occupied in the nonannealed sample, corresponding to the compositions  $\text{Ba}_2\text{YCu}_3\text{O}_{7.0}$  and  $\text{Ba}_2\text{YCu}_3\text{O}_{6.8}$ , respectively (the difference of 0.2 in the oxygen content between the two samples has been confirmed by differential thermal gravimetric analysis). The copper

atom Cu(1) is located at the center of a near rectangle formed by two O(4) atoms at a distance of 1.9429(1) Å (the distances used in this discussion refer to the annealed phase measured at room temperature) and two O(1) atoms at a distance of 1.846(2) Å. These near rectangles are connected by vertices and form chains along the *b* axis. In the nonannealed compound about 20% of the O(4) sites are vacant, resulting in a significantly defective structure along the chains Cu(1)-O(4), while they are fully occupied in the annealed compound. The copper atom Cu(2) is also surrounded by four oxygen atoms with distances Cu(2)-O(2)=1.9299(4) Å and Cu(2)-O(3)=1.9607(4) Å. The four atoms are almost exactly coplanar, and the Cu(2) atom is slightly removed from the plane (about 0.28 Å) toward the nearest O(1) atom along the *c* axis at a distance of 2.295(3) Å. This pyramidal configuration is outlined in Fig. 1.

In conclusion, neutron powder diffraction analysis has allowed us to derive the correct location of the oxygen atoms in the superconductor  $\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$  and to determine the atomic coordinates of all atoms with a precision far better than that obtained in the single-crystal x-ray diffraction studies. The symmetry is established as orthorhombic, space group *Pmmm*. No detectable changes of structure have been observed in going from room temperature to 10 K. A significant result of this study is that the sites of the oxygen atoms O(4) are fully occupied in the annealed phase, and have 20% vacancies in the nonannealed phase.

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FIG. 1. Perspective view of the unit cell of  $\text{Ba}_2\text{YCu}_3\text{O}_7$ .

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