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# Crystallographic description of phases in the Y-Ba-Cu-O superconductor

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Single-crystal x-ray techniques were used to determine two structures that comprise the Y-Ba-Cu-O superconductor. A green phase has the orthorhombic $Y_2BaCuO_5$ structure. An opaque phase ($YBa_2Cu_3O_{6+x}$, $0 \leqq x \leqq 1.0$) is tetragonal ($a = 3.859$ Å, $c = 11.71$ Å; space group $P\bar{4}m2$; $Z = 1$). The structure is related to a 1:1:3 $ABO_3$ perovskite: Ba and Y order in $A$ sites and Cu is in $B$ sites. Systematic oxygen vacancies between adjacent copper atoms lead to a fourfold-coordinate Cu in proximity to Y and a twofold-coordinate Cu in the vicinity of the Ba site.

Wu *et al.*[1] described superconductivity at 93 K in a mixed-phase Y-Ba-Cu-O compound system. Their preliminary x-ray powder studies of the multiphase assemblage produced a pattern that differed from other known superconducting structures. In order to understand the origin of the extraordinary properties of this material it is essential to document the atomic structures of the phases that comprise the mixture. We have used single-crystal x-ray diffraction techniques to examine the original material described by Wu *et al.* (batch 1), as well as additional Y-Ba-Cu-O superconducting samples synthesized at the University of Houston (batch 2). The latter sample exhibits 100% superconductivity by ac susceptibility measurements. In this Rapid Communication we identify the two phases that comprise at least 95% of the sample volume and describe their novel crystal structures.

Optical examination of the greenish-black, polycrystalline material revealed opaque grains up to about 30 $\mu$m diameter and transparent green particles of average size 5 to 10 $\mu$m. Samples from two batches of this synthetic material were polished for chemical analysis with an electron microprobe. The ratio of green phase to opaque phase is 2:1 for batch 1 and 1:3 for batch 2. A JOEL scanning-electron-microscope (SEM) probe was used in the wavelength dispersive mode; beam conditions were 15 kV and 10 nA. The $K$ line of copper and $L$ lines of barium and yttrium were used. The reference standards were barium silicate glass and pure metallic copper and yttrium. Eight grains of both green and opaque phases were analyzed; two discrete compositions corresponded to these two types of grains. The Ba:Cu:Y cation ratios for the green phase are $0.495 \pm 0.017$:$0.490 \pm 0.029$:1; we assume a stoichiometric composition of $Y_2BaCuO_5$. Ba:Cu:Y cation ratios for the black phase are $2.08 \pm 0.08$:$2.85 \pm 0.10$:1, corresponding to an approximate formula of $YBa_2Cu_3O_{6+x}$ ($x \approx 0.5$). The valence of copper, and thus the exact number of oxygen atoms per formula unit, is not known. The opaque black appearance of the sample is consistent with charge-transfer effects between $Cu^+$ and $Cu^{2+}$ or between $Cu^{2+}$ and $Cu^{3+}$.

Densities of the two phases were determined by Dr. John Marinenko with a micropycnometer.[2] A 14-mg sample of the opaque phase and a 17-mg sample of the green phase were used. The average densities were $5.65 \pm 0.05$ g/cm$^3$ for the green phase and $5.93 \pm 0.22$ g/cm$^3$ for the opaque phase. Since the material is porous the true density could be as much as 10% greater.

The green phase has the orthorhombic $A_2BaCuO_5$ structure ($A$ is Y or a rare-earth element), which was described on the basis of powder x-ray diffraction by Michel and Raveau.[3] We confirmed the structure of the green phase on an unusually large particle with irregular shape approximating a flat triangular plate 10 $\mu$m thick and 30 $\mu$m on edge. Unit-cell dimensions were determined on an automated four-circle x-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

Intensity data were collected from two octants of reciprocal space to $\sin\theta/\lambda = 0.7$. We collected 1020 reflections, which were corrected for the extremely strong absorption effects ($\mu_l = 324$ cm$^{-1}$), and averaged to yield a total of 548 nonequivalent structure factors. Michel and Raveau refined their powder data in space group *Pbnm*; however, we observe several weak violations of the $b$ glide ($0kl$ reflections with $k$ odd), suggesting a lower symmetry space group with diffraction symbol $mmmP \cdot n \cdot$, which allows the structure to belong to one of four possible space groups. Only one of these, $P2_1nm$, yields a structure consistent with the *Pbnm* supersymmetry and crystal chemical constraints. We refined the structure in both space groups and equally good fits to the intensity data were obtained, with no significant difference between the two sets of positional parameters.

Structural parameters are reported in Table I for the ideal stoichiometric composition of the green phase, $Y_2BaCuO_5$, in space group *Pbnm*. Our refined positional parameters differ in some details from those of Michel and Raveau, with the result that our structure has more reasonable Cu-O distances. In the $Y_2BaCuO_5$ structure (Fig. 1) all of the cations reside in layers which are stacked at 2.82-Å intervals along the $c$ axis of the structure. These cation layers are coordinated by oxygen anions that form layers interleaved with those of the cations, plus an additional oxygen in the metal cation plane. Each yttrium atom is sevenfold coordinated by a capped

TABLE I. Atomic coordinates for $Y_2BaCuO_5$ in space group *Pbnm*.

| Atom | Multiplicity | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|
| Ba | 4 | 0.93 | 0.90 | 0.25 |
| Y-1 | 4 | 0.12 | 0.29 | 0.25 |
| Y-2 | 4 | 0.40 | 0.07 | 0.25 |
| Cu | 4 | 0.71 | 0.66 | 0.25 |
| O-1 | 8 | 0.16 | 0.43 | 0.00 |
| O-2 | 8 | 0.36 | 0.23 | 0.50 |
| O-3 | 4 | 0.03 | 0.10 | 0.25 |

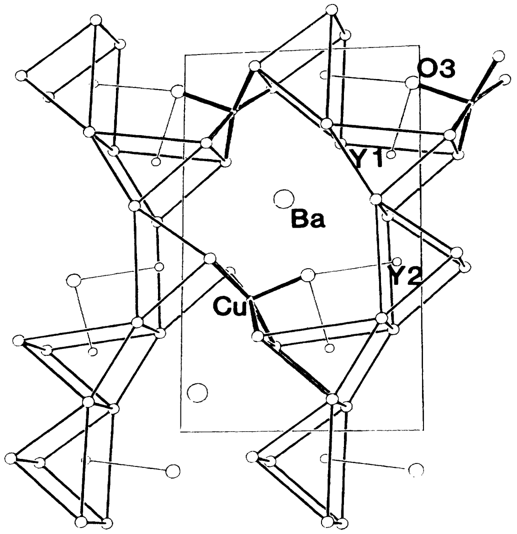

FIG. 1. The crystal structure of $Y_2BaCuO_5$ in approximate *c*-axis projection. Only one layer of cation polyhedra, at $z=\frac{1}{4}$, is shown. The oxygen atoms O-1 and O-2, which coordinate these sites, lie at heights $z=0$ and $z=\frac{1}{2}$.

trigonal prism of oxygen atoms; these prisms share edges to form chains parallel to the *b* axis. Chains are cross linked by copper atoms in fivefold-coordinated square pyramids of oxygen atoms, and by barium atoms which reside in larger, elevenfold coordinated sites (Table II). Consecutive layers of cations are not stacked directly above one another, but are displaced by the *n* glide, so that instead of sharing end faces the trigonal prisms are stacked with shared edges.

Electron microprobe analyses of the green phase cannot rule out slight deviations from stoichiometry. For example, a removal of $\frac{1}{8}$ of the yttrium atoms (and sufficient oxygens to maintain charge balance) would result in a calculated density of 5.8 g/cm$^3$, compared with the measured density of 5.65 g/cm$^3$. The removal of some cations at random from the structure would still be consistent with our structure solution, which is relatively insensitive to the exact content of the cation sites. The weak reflections that violate the *b* glide of *Pbnm* may arise from deviations from the ideal stoichiometry of $Y_2BaCuO_5$. Such deviations could give rise to an ordered derivative structure of symmetry lower than the ideal *Pbnm*.

Opaque-phase unit-cell parameters were initially determined on a subsequent 50-$\mu$m-diam fragment from batch 1; all diffraction maxima were broad and several were split, indicative of twinning. Preliminary unit-cell refinements were based on a pseudocubic lattice with $a=3.9$ Å; only body-centered-type reflections were observed, consistent with a perovskitelike structure with all metal cations on center or corner positions. A better crystal from batch 2, approximately $50\times40\times20$ $\mu$m$^3$, was employed for precise unit-cell determination. The pseudocubic subcell was found to have a slight tetragonal distortion, with $a=3.859\pm0.003$ Å and $c=3.904\pm0.001$ Å. Slow diffractometer scans for supercell reflections based on both five- and six-cell repeats of both the *a* and *c* axes were made for all reflections to $\sin\theta/\lambda=0.35$. Many moderately strong reflections of the type $h,k,l/3$ were observed, but no other superstructure was detected. We thus rule out superstructures of 2, 4, 5, or 6 subcells along either axis, but the *c* axis is tripled.

Additional unit-cell dimensions were determined on two crystals from batch 1 and three from batch 2; small but significant differences are observed. Batch 1 opaque

TABLE II. Selected interatomic distances in $Y_2BaCuO_5$ in space group *Pbnm*.

| Atoms | $d$ (Å) | Multiplicity | Atoms | $d$ (Å) | Multiplicity |
|---|---|---|---|---|---|
| Ba–O-1 | 3.28 | 2 | Cu–O-1 | 2.01 | 2 |
| Ba–O-1 | 3.15 | 2 | Cu–O-2 | 2.01 | 2 |
| Ba–O-2 | 2.99 | 2 | Cu–O-3 | 1.99 | 1 |
| Ba–O-2 | 2.96 | 2 | Y-1–Cu | 3.14 | 2 |
| Ba–O-3 | 2.83 | 2 | Y-1–Cu | 2.83 | 1 |
| Ba–O-3 | 2.47 | 1 | Y-2–Cu | 2.97 | 1 |
| Y-1–O-1 | 2.22 | 2 | Y-1–Y-2 | 3.28 | 1 |
| Y-1–O-2 | 2.33 | 2 | Y-1–Y-2 | 3.47 | 1 |
| Y-1–O-2 | 2.34 | 2 | Ba–Cu | 3.26 | 1 |
| Y-1–O-3 | 2.38 | 1 | Ba–Cu | 3.37 | 1 |
| Y-2–O-1 | 2.29 | 2 | | | |
| Y-2–O-1 | 2.33 | 2 | | | |
| Y-2–O-2 | 2.39 | 2 | | | |
| Y-2–O-3 | 2.59 | 1 | | | |

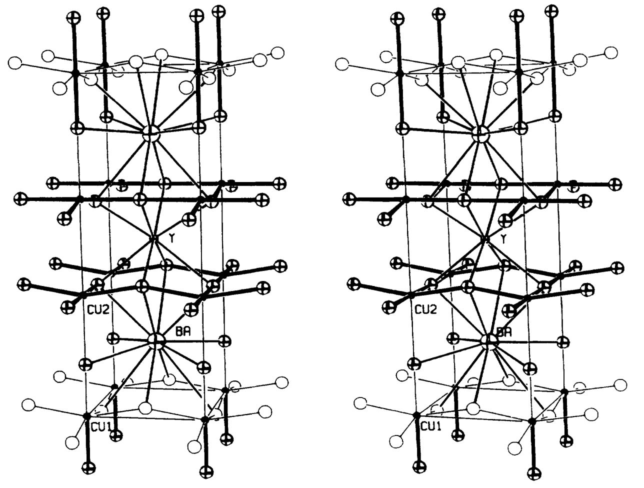

FIG. 2. Stereographic view of the crystal structure of $YBa_2Cu_3O_{6+x}$. The tetragonal structure has Ba and Y in cubic eightfold coordination and Cu in twofold and fourfold coordination. The oxygen positions, denoted by open circles, are essentially vacant.

phase has an average cell of $a_1 = a_2 = 3.859 \pm 0.003$ and $c = 11.71 \pm 0.01$ Å, whereas batch 2 has $a_1 = 3.848 \pm 0.001$, $a_2 = 3.854 \pm 0.001$ and 11.746 Å. Note that the batch 2 crystals deviate slightly from tetragonal dimensionality. The effects of opaque phase compositional variation, particularly the variation of $f_{O2}$ at synthesis, may be critical in causing slight deviations from tetragonal supersymmetry.

Intensity data were collected on a fragment from batch 2, approximately $25 \times 30 \times 35$ $\mu m^3$, that appears untwinned on the basis of unsplit diffraction maxima. We obtained 980 integrated intensities from one quadrant of reciprocal space to $\sin\theta/\lambda = 0.6$. Reflections were corrected for crystal absorption ($\mu_l = 254$ cm$^{-1}$) and averaged to yield 130 symmetrically independent structure factors with an internal agreement of 9%. No systematic absences were noted in this data set, which is consistent with a Laue-symmetry class of $4/mmm$ and diffraction symbol $4/mmmP\cdots$.

Patterson maps indicate a perovskitelike distribution of cations. Significant differences in atomic number of the three metals facilitate an unambiguous assignment of ordered cation positions. Only one cation distribution model (Fig. 2) yields a solution with reasonable cation temperature factors and occupancies. Barium and yttrium cations are in an ordered Ba-Y-Ba sequence along $[\frac{1}{2}\ \frac{1}{2}\ z]$, while copper atoms occur at $(0,0,z)$. This distribution of metal atoms, even with no oxygens included in the refinement, results in a residual of under 15%. Different Fourier techniques were employed to locate oxygen atoms, each of which accounts for less than 5% of the total electron density. Features at (0,0,0.15), $(\frac{1}{2},0,0.38)$, and $(\frac{1}{2},0,0.61)$ correspond to six oxygen atoms per unit cell. A feature at $(\frac{1}{2},0,0)$ is much smaller than other oxygen positions. There is no evidence for oxygen at the face-centered ("NaCl-type") oxygen positions, nor is there an electron density maximum at (0,0,0.50) adjacent to the Y cation. The separation of two copper cations above and below the Y layer is only 3.2 Å, too short for an intermediate oxygen.

TABLE III. Atomic coordinates for $YBa_2Cu_3O_{6+x}$ in space group $P\bar{4}m2$.

| Atom | Multiplicity | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|
| Ba | 2 | 0.50 | 0.50 | 0.19 |
| Y | 1 | 0.50 | 0.50 | 0.50 |
| Cu-1 | 1 | 0.00 | 0.00 | 0.00 |
| Cu-2 | 2 | 0.00 | 0.00 | 0.36 |
| O-1[a] | 2 | 0.50 | 0.00 | 0.03 |
| O-2 | 2 | 0.50 | 0.00 | 0.38 |
| O-3 | 2 | 0.50 | 0.00 | 0.61 |
| O-4 | 2 | 0.00 | 0.00 | 0.15 |

[a] This oxygen site may be only partially occupied.

The diffraction symbol $4/mmmP\cdots$, as well as the cation-anion topology described above, is consistent with six different space groups. An $N(Z)$ test of the structure factor data indicates that the correct space group is noncentric. Refinement in space group $P4mm$ yields the lowest residual; however, the isotropic temperature factors are not well conditioned. We have tentatively concluded, therefore, that the space group is $P\bar{4}m2$. Refined values of positional parameters (weighted residual $\approx 6\%$) appear in Table III; selected interatomic distance are in Table IV. Note that in this space group the oxygens sur-

TABLE IV. Selected interatomic distances in $YBa_2Cu_3O_{6+x}$ in space group $P\bar{4}m2$.

| Atoms | $d$ ($A$) | Multiplicity | Atoms | $d$ ($A$) | Multiplicity |
|---|---|---|---|---|---|
| Ba–O-1 | 2.77 | 2 | Cu-2–O-2 | 1.95 | 2 |
| Ba–O-1 | 3.15 | 2 | Cu-2–O-3 | 1.94 | 2 |
| Ba–O-2 | 2.95 | 2 | Cu-2–O-4 | 2.43 | 2 |
| Ba–O-3 | 2.93 | 2 | | | |
| Ba–O-4 | 2.77 | 4 | Cu-1–Cu-2 | 3.30 | 1 |
| Y–O-2 | 2.37 | 4 | Cu-1–Cu-2 | 4.20 | 2 |
| Y–O-3 | 2.39 | 4 | | | |
| Cu-1–O-1 | 1.95 | 4 | Y–Cu-2 | 3.19 | 4 |
| Cu-1–O-4 | 1.78 | 2 | | | |

rounding each copper are not constrained to adopt regular coordination; distortions are observed for both Cu-1 and Cu-2 (Fig. 2). Refinement of occupancy factors indicate no scattering density at (0.5,0,0), whereas the other oxygen positions are completely occupied.

Systematic absences of oxygen atoms lead to an unusual arrangement in which Cu-2 is coordinated by four oxygen atoms and Cu-1 by two oxygen atoms, similar to the arrangement found for $Cu^{1+}$ in $Cu_2O$. The Y cation has cubic eightfold coordination and Ba has a distorted eightfold coordination. This structure appears to be related to that of $La_3Ba_3Cu_6O_{14}$, which was reported by Er-Rakho, Michel, Provost, and Raveau to have square-planar copper and eightfold-coordinated Ba and trivalent cations on the basis of powder data.[4] Their proposed structure, in addition, had Cu in five- and sixfold coordination alternating with the square-planar arrays. Reexamination of their intensity data, however, indicates that the actual structure of $La_3Ba_3Cu_6O_{13}$ is probably the same as that of the superconducting opaque phase described here.

While the basic elements of this new proposed structure appear to be correct, there are several possible structural variations that cannot be resolved with our present data. For example, we can accommodate any intermediate structural formula between stoichiometric, fully ordered end members

$$(YBa_2)(Cu^{+}Cu^{2+}{}_2)O_6$$

and

$$(YBa_2)(Cu^{2+}{}_2Cu^{3+})O_7 .$$

Partial occupancy of oxygen at (0.5,0,0) is possible; therefore, local domains with capped square-planar coordination of $Cu^{3+}$ in Cu-1 are possible. Furthermore, the exact cation ratio may deviate from that of the ideal formula; we cannot preclude some cation disorder such as Ba↔Y or Cu↔Y effects. Such partial occupancy, ordering, and defect details will undoubtedly affect the electronic properties of this perovskite-related phase. Additional single-crystal studies are now in progress to resolve some of these structural subtleties.

*Note added.* Analysis of our unusually broad diffraction peak shapes indicates that the tetragonal superconducting material is characterized by small domains, on the order of perhaps 100 Å. We suggest that our observed tetragonal average structure is a consequence of rapid quenching of a sample that crystallized in tetragonal space group $P4/mmm$ or $P\bar{4}m2$ at high temperature, and was then rapidly cooled through a tetragonal-to-orthorhombic transition. Separate orthorhombic domains, much too small to be resolved by x-ray techniques, are related by merohedral twin laws that are symmetry operators lost during the transition; i.e., 4 rotation, $\bar{4}$ rotation, etc. Sample annealing should result in significantly larger twin domains and orthorhombic x-ray diffraction symmetry. High-temperature x-ray diffraction experiments are in progress; heating-stage transmission electron microscope experiments would also be helpful in resolving details of the proposed transition.

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