

Combined X-Ray and Neutron Powder Diffraction Study of the Structure of $\text{Ba}_4\text{CaCu}_3\text{O}_x$: Oxygen Stoichiometry and Cation Order*

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Received November 27, 1991; accepted March 5, 1992

Cation ordering and oxygen stoichiometry of the nonsuperconducting compound, $\text{Ba}_4\text{CaCu}_3\text{O}_x$, have been studied by a joint X-ray and neutron powder diffraction experiment. In contrast to the related phase $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$, which was refined in the space group $Pm\bar{3}$, we found that the higher symmetry space group $Im\bar{3}m$ provides a better fit to the diffraction data for $\text{Ba}_4\text{CaCu}_3\text{O}_x$. The cubic unit cell of $\text{Ba}_4\text{CaCu}_3\text{O}_x$ has a perovskite-like configuration, but possesses lattice lengths double those of a usual perovskite cell. X-ray scattering data clearly show substantial exchange between the Ca and Ba sites. Refinements of neutron data indicate two oxygen sites: an $(x, 0, 0)$ site that is essentially fully occupied and a $(\frac{1}{4}, 0, \frac{1}{2})$ site that is approximately 47% occupied. The joint X-ray and neutron refinement yields an average stoichiometry of $\text{Ba}_{3.92}\text{Ca}_{1.08}\text{Cu}_3\text{O}_{8.85}$ for the compound ($Z = 2$) and an effective Cu–O hole concentration of +0.29. $\text{Ba}_{3.92}\text{Ca}_{1.08}\text{Cu}_3\text{O}_{8.85}$ is a dielectric; the absence of superconductivity in this material is discussed in terms of its structure and oxygen stoichiometry. © 1992 Academic Press, Inc.

Introduction

During the course of a study of the Ba–Ca–Cu–oxide phase diagram, we synthesized and characterized the new phase $\text{Ba}_4\text{CaCu}_3\text{O}_x$ (1). A preliminary structure, based on a single-crystal X-ray diffraction study, was initially indexed to a cubic unit cell with a refined lattice constant of 4.086(6) Å. This structure consisted of a cube of Ba atoms with a disordered Ca/Cu atom located at the cube center. As a consequence of the

Ca/Cu disorder, the possibility of an ordered supercell for the compound was considered. Close examination of axial photographs of the crystal revealed faint spots consistent with an 8-Å cubic unit cell and a possible ordering of the Ca and Cu sites. Unfortunately, we were not able to collect sufficient data from the crystal to refine the structure in this larger, presumably ordered, cell.

The existence of an 8-Å cell for $\text{Ba}_4\text{CaCu}_3\text{O}_x$, coupled with the similarity of its chemical formula to that of $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$, suggests that the structures of these two compounds should be related. Structural refinements of $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ have been carried out using both powder X-ray (2) and powder neutron (3) diffraction. These two

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separate studies refined the structure in the same space group ($Pm3$, $a = 8.12 \text{ \AA}$, $Z = 2$) and found the same heavy atom framework, but differed slightly in oxygen placement and occupancy. The neutron refinement (3) of $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ revealed a structure composed of oxygen-linked CuO_6 and YO_6 octahedral groups. Unit-cell corners are YO_6 units that share oxygens with edge-centered CuO_6 groups. A YO_6 unit is also positioned in the center of the cell; this YO_6 shares oxygens with CuO_6 octahedra located on the cell faces. The Ba atoms reside in perovskite-like subcubes, the corners of which consist of two YO_6 and six CuO_6 oxygen-sharing octahedra. At the $\delta = 0.0$ and 0.5 values of the oxygen stoichiometry, the hole concentration (p) per Cu–O unit is $+0.00$ and $+0.17$, respectively.

We have carried out a detailed joint X-ray and neutron powder diffraction study of $\text{Ba}_4\text{CaCu}_3\text{O}_x$. Since our preliminary description of this phase (4), Abbattista *et al.* (5) have reported an X-ray structural refinement of $\text{Ba}_4\text{CaCu}_3\text{O}_x$. Our work goes beyond that of Abbattista and co-workers in that we explored the degree of cation ordering and oxygen content and stoichiometry of $\text{Ba}_4\text{CaCu}_3\text{O}_x$. In our investigation, neutron data provided most of the structural information desired; however, since the neutron scattering lengths for Ba and Ca are similar, X-ray data were used in conjunction with the neutron data to study the extent of cation ordering between Ba and Ca (6, 7).

$\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ does not display superconductivity to 7 K. The phase $\text{Ba}_4\text{CaCu}_3\text{O}_x$ can be considered a hole-doped form of $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ because of the complete substitution of Y^{+3} in $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ by Ca^{+2} in $\text{Ba}_4\text{CaCu}_3\text{O}_x$. Even though hole doping is not the only criterion for the creation or enhancement of superconductivity (8), we checked for superconductivity in $\text{Ba}_4\text{CaCu}_3\text{O}_x$. $\text{Ba}_4\text{CaCu}_3\text{O}_x$ also does not display superconductivity to 7 K. An estimation of the oxygen content of $\text{Ba}_4\text{CaCu}_3\text{O}_x$ and a

comparison of its structure with that of $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ is thus especially interesting because it is possible that the absence of superconductivity in both of these perovskite-related systems is related to structural constraints or to oxygen deficiencies.

Experimental Details

Bulk samples of $\text{Ba}_4\text{CaCu}_3\text{O}_x$ were prepared by heating stoichiometric quantities of BaO_2 , CaO , and CuO at 965°C in O_2 for 24 hr. Samples were cooled in O_2 from 965°C to room temperature over a 5-hr period. $\text{Ba}_4\text{CaCu}_3\text{O}_x$ is an insulator and so magnetic susceptibility measurements of this sample to a temperature of 7 K did not show superconductivity.

Neutron powder diffraction data were taken on the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. Structural models were refined using the Rietveld refinement code developed by Larson and Von Dreele (9). Data collected using the $\pm 153^\circ$ and the $\pm 90^\circ$ detector banks and covering a d -spacing range from 0.4 to about 6.6 \AA were used in the structural refinements. A portion of these data is displayed in Fig. 1a. Because we were interested in cation ordering and because the neutron scattering lengths for Ca and Ba are similar (4.90 and 5.35 fm, respectively), an X-ray data set was collected on another portion of the same sample. Powder X-ray diffraction data, part of which is shown in Fig. 1b, were taken at a sample temperature of 300 K using a Scintag XDS2000 diffractometer with $\text{Cu } K\alpha$ radiation in a single scan ($20^\circ < 2\theta < 150^\circ$) using 0.02° steps and counting for 8 sec per step. The data showed that an impurity phase was present; the diffraction pattern for this phase corresponded to that of BaCuO_2 .

A two-phase refinement, which took into account the BaCuO_2 impurity, was carried

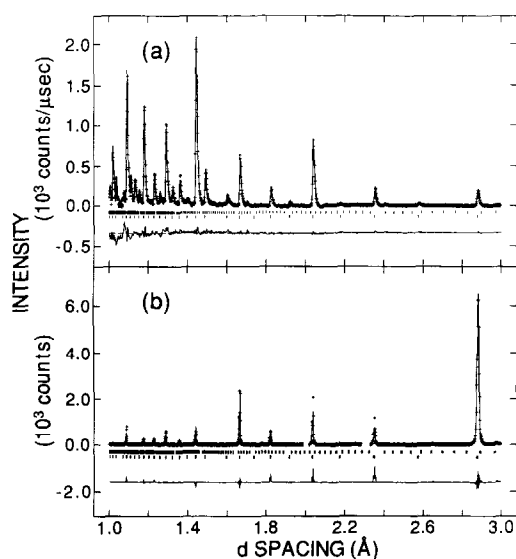


FIG. 1. Part of the powder diffraction data for $\text{Ba}_{3.92}\text{Ca}_{1.08}\text{Cu}_3\text{O}_{8.85}$ at 300 K. Panel (a) represents neutron powder diffraction data. Data shown by plus (+) marks were collected on the $+153^\circ$ detector bank of the High Intensity Powder Diffractometer at LANSCE. Panel (b) shows X-ray powder diffraction collected with a Scintag XDS2000. Two regions in the X-ray pattern near $d = 2.0$ and 2.3 \AA , which included Bragg reflections from the aluminum sample holder, were excluded. Tick marks below the data indicate the positions for the allowed reflections for $\text{Ba}_{3.92}\text{Ca}_{1.08}\text{Cu}_3\text{O}_{8.85}$ (lower marks) and for BaCuO_2 (upper marks). Both $\text{Cu}K\alpha_1$ and $\text{Cu}K\alpha_2$ positions are marked in the X-ray pattern; the d spacings are computed from $K\alpha_1$. The continuous line through the data is the calculated profile from Reitveld refinements. The lower curve in each panel represents the difference between the observed and calculated profiles.

out. The structural model for $\text{Ba}_4\text{CaCu}_3\text{O}_x$ was refined for lattice parameters, atomic positions, anisotropic thermal parameters, cation order for the Ca and Ba atoms, and occupancy of the oxygen sites. Background coefficients, scale factor, diffractometer constants for the $\pm 153^\circ$ and $\pm 90^\circ$ detector banks, isotropic strain in the profile coefficients, sample absorption (neutron), Lorentzian and Gaussian line shape terms (X-ray), sample height (X-ray), and peak asymmetry (X-ray) were also refined. X-ray

scattering factors for the cations Ca^{2+} , Ba^{2+} , and Cu^{2+} were used; similar scattering factors for O^{2-} were not available, so those corresponding to the neutral atom were used. The lattice constants and isotropic profile coefficients for the impurity BaCuO_2 phase were also refined. The scale factor corresponding to this latter phase was small (0.009), but because the unit cell for BaCuO_2 is very large, it accounted for 17.6 wt% of the sample. Since no other phases were present, we can calculate the relative amounts of Ba and Ca in $\text{Ba}_4\text{CaCu}_3\text{O}_x$. The starting Ba : Ca ratio was known to be 4, and since no solid solutions corresponding to $(\text{Ca}, \text{Ba})\text{CuO}_2$ are known at the synthesis temperature we used for $\text{Ba}_4\text{CaCu}_3\text{O}_x$ (10), we assume that the Ca appears only in the primary $\text{Ba}_4\text{CaCu}_3\text{O}_x$ phase. The amount of BaCuO_2 impurity then suggests that the $\text{Ba}_4\text{CaCu}_3\text{O}_x$ phase is more accurately represented by the formula $\text{Ba}_{3.92}\text{Ca}_{1.08}\text{Cu}_3\text{O}_x$. Subsequent structural refinements for $\text{Ba}_{3.92}\text{Ca}_{1.08}\text{Cu}_3\text{O}_x$ took into account this Ba : Ca ratio.

Results and Discussion

Initially, an attempt was made to fit the data using the space group $Im\bar{3}m$ with lattice constant $a = 4.086 \text{ \AA}$ and with Ba atoms at the cell corners, a disordered Ca/Cu atom at the cell center, and the oxygen atoms located at face centers (1). This choice of a unit cell, however, did not account for a number of reflections present in the neutron and X-ray data. Use of the space group $Pm\bar{3}$ (utilized for $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$ (2, 3) and the X-ray structure of $\text{Ba}_4\text{CaCu}_3\text{O}_x$ (5)) with doubled lattice lengths of approximately 8 \AA , initially provided a much better fit to both the X-ray and neutron data, but ultimately resulted in refinements that were unstable in atomic positions, site occupancies, and thermal parameters. In particular, we noticed that the Ba atom site would oscillate around the (x, x, x) position with $x = 0.25$,

TABLE I
STRUCTURAL PARAMETERS AT 300 K
FOR Ba_{3.92}Ca_{1.08}Cu₃O_{8.85}

Parameter	Refined value
<i>a</i> (Å)	8.1398(1)
<i>V</i> (Å ³)	539.32(2)
Ca/Ba <i>f</i>	0.637(8)/0.363(8)
<i>U</i> _{iso}	3.88(12)
Ba/Ca <i>f</i>	0.889(2)/0.111(2)
<i>U</i> _{iso}	1.38(2)
Cu <i>f</i>	1
<i>U</i> _{iso}	0.87(2)
O(1) <i>f</i>	1
<i>x</i>	0.28014(13)
<i>U</i> ₁₁	0.48(5)
<i>U</i> ₂₂ = <i>U</i> ₃₃	4.27(5)
O(2) <i>f</i>	0.474(3)
<i>U</i> ₁₁	5.68(18)
<i>U</i> ₂₂ = <i>U</i> ₃₃	1.24(6)
<i>R</i> _{wp} / <i>R</i> _{exp} :	
Neutron	2.69/2.03
X-ray	16.11/11.77
<i>d</i> -spacing range:	
Neutron	0.4–6.0 Å
X-ray	0.7–7.5 Å

Note. Space group *Im3m*: Ca/Ba (0, 0, 0), Ba/Ca ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), Cu (0, $\frac{1}{2}, \frac{1}{2}$), O1 (*x*, 0, 0), and O2 ($\frac{1}{4}, 0, \frac{1}{2}$). Numbers in parentheses following refined parameters are standard deviations in the last significant digit(s) (thermal parameters are in units of 100 Å², agreement factors are in percent).

suggesting that the correct space group should place the Ba atom in the special position ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$). Employment of the higher symmetry space group *Im3m* (*Z* = 2) with a refined lattice parameter *a* = 8.1398(1) Å and placement of the Ba atoms at the special position of ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) gave both a good fit and stable refinements. This structure fixed the Ca atoms at the center and corners of the cubic cell, and the Cu atoms at each cube face center and halfway along each cube edge. The heavy atom framework is analogous to that previously discussed for Ba₄YCu₃O_{8.5+δ}, except for the positioning of the Ba atoms in a special site. Oxygen occupies

only two distinct locations in the cell, one at (*x*, 0, 0) and one at ($\frac{1}{4}, 0, \frac{1}{2}$). Structural parameters for Ba₄CaCu₃O_{*x*} are listed in Table I and an ORTEP (11) plot of the structure is shown in Fig. 2.

When the Ca and Ba atom occupancies were refined with only the neutron data, the site occupancies refined to 0.918(16) and 0.979(5), respectively. However, when the thermal parameters were fixed at the values obtained with the neutron data, and the Ca and Ba atoms occupancies were refined jointly with both neutron and X-ray data, the population factors converged to the values of 1.203(34) and 0.843(6) for Ca and Ba, respectively. If a full site occupancy of 1.0 is assumed, these population factors suggest that the Ca atom shares its site with an atom that has a larger X-ray scattering factor than that of Ca, and that the Ba atom shares its site with an atom that has a smaller X-ray scattering factor than that of Ba. Accordingly, Ba atoms were mixed into the Ca site and Ca atoms were mixed into the Ba site. Each site occupancy was constrained to unity and the overall Ba/Ca stoichiometry constrained to the 3.92:1.08 ratio. The occupancy factors for the mixed Ca/Ba and

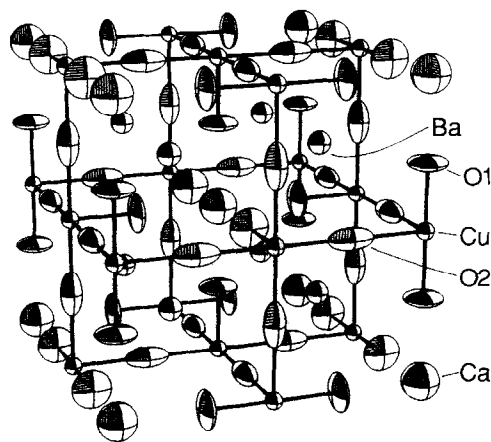


FIG. 2. ORTEP plot of the structure of Ba_{3.92}Ca_{1.08}Cu₃O_{8.85} at 300 K. The thermal ellipsoids are drawn to represent 95% probability surfaces.

Ba/Ca sites were then refined to give the extent of site disorder. The population values converged to yield a Ca site containing approximately 40% Ba and a Ba site containing approximately 10% Ca. Despite the apparent lack of solubility of Ca in BaCuO₂ (10) at higher synthesis temperatures, a mutual solubility of Ca and Ba has previously been observed in a doped BaTiO₃ system (12) and in a YBa_{2-x}Ca_xCu₄O_{8+y} system (13). This joint Ca/Ba site occupancy in Ba₄CaCu₃O_x suggests that the point occupied by Ba₄CaCu₃O_x in the Ba–Ca–Cu–oxide phase diagram is actually a region of variable Ca and Ba composition.

Of the two oxygen sites in Ba_{3.92}Ca_{1.08}Cu₃O_{8.85}, the one at (x, 0, 0) is essentially fully occupied while the one at ($\frac{1}{4}$, 0, $\frac{1}{2}$) is only partially occupied with a population factor of 0.474(3). This gives an oxygen composition of x = 8.85 for Ba_{3.92}Ca_{1.08}Cu₃O_{8.85} and an average valence of +2.57 per copper atom. Charge balance then gives a hole concentration of p = +0.29 per [CuO₂] unit for Ba_{3.92}Ca_{1.08}Cu₃O_{8.85}. This value lies between those for YBa₂Cu₃O_{6.5+δ} (p = +0.50, assuming holes are located in the CuO₂ sheets) (14) and the cation- and oxygen-doped La₂CuO₄ systems (p = +0.15–+0.18) (15). Thus, a superficial comparison of these compounds indicates that hole concentration is not the only consideration for superconductivity. The absence of superconductivity in Ba_{3.92}Ca_{1.08}Cu₃O_{8.85} and in Ba₄YCu₂O_{8.5+δ} must be attributed to other factors such as structural constraints or oxygen deficiencies.

As can be seen in Fig. 2, Ba_{3.92}Ca_{1.08}Cu₃O_{8.85} has a cubic Cu–O network consisting of CuO₆ octahedra with “isolated” O1 atoms and edge-shared O2 atoms. The length of 2.035 Å for the Cu–O2 bond is imposed by the size of the lattice and is much larger than the typical Cu–O length of 1.93 Å found in most cuprates. On the other hand, the Cu–O1 bond is quite short (1.790 Å). Thus, these CuO₆ octahedra have an

oblate shape rather than the more commonly found prolate shape, as, for example, in the doped La₂CuO₄ compounds (16). This distinction indicates a difference in Cu–O bonding from that found in doped La₂CuO₄. For Ba_{3.92}Ca_{1.08}Cu₃O_{8.85}, the Cu–O1 bonds contain much greater charge density than the Cu–O2 bonds, and the holes appear to be localized in the Cu–O1 bonds. Thus there are at least two obstacles to superconductivity in Ba_{3.92}Ca_{1.08}Cu₃O_{8.85}: the large size of the Ba²⁺ ions constrains the Cu–O2 bond distance to a length that is perhaps too long for hole doping (17), and the proximity of the Ca²⁺ to the O1 oxygens helps stabilize the holes on the latter.

Another pronounced feature detrimental to superconductivity is the 53% vacancy in the O2 sites. Normally, this would be enough to disrupt the connectivity between adjacent Cu–O units, but here the situation is perhaps even worse: the shapes of the thermal parameters for O2, elongated down the Cu–O2 bonds, suggest that the oxygens in these sites are actually disordered and not shared equally by CuO₆ octahedra. A more realistic picture of the structure may involve Cu(O1)₄ square planes that are weakly joined by the O2 atoms to adjacent Cu(O1)₄ square planes. These structural features suggest that even an increase in the oxygen content of Ba_{3.92}Ca_{1.08}Cu₃O_{8.85} may not provide the continuous O–Cu–O chains needed for superconductivity.

Finally, the similarity in the structures of Ba_{3.92}Ca_{1.08}Cu₃O_{8.85} and Ba₄YCu₃O_{8.5+δ}, and our finding that the structure of the former is characterized by the space group *Im3m* instead of *Pm3*, raises the question of whether the space group *Im3m* may also be more appropriate for the latter. This is a question we hope to address later.

Acknowledgments

The Manuel Lujan, Jr., Neutron Scattering Center is funded in part by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials

Sciences. This work was done under the auspices of the U.S. Department of Energy and was funded by the High Temperature Superconductor Institutional Research Initiative Program at Los Alamos National Laboratory.

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