Neutron Diffraction Study of the Nonmodulated 2212-Type Cuprate $Bi_{1.5}Ba_{2.5}LaCu_2O_{8.25}$

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The structure of the nonmodulated bismuth cuprate $Bi_{1.5}Ba_{2.5}La$ $Cu_2O_{8.25}$ has been determined from powder neutron diffraction data. This phase crystallizes in the space group *I4/mmm*, with $a = 3.9322(1)$ and $c = 31.240(1)$ Å. The significant features are: (i) the puckering of the $[CuO_2]_\infty$ layers due to the fact that copper is located out of the basal plane of the CuO_5 pyramid, (ii) the location of barium in the bismuth bilayers, whereas lanthanum occupies entirely the fluorite-type cages between the copper layers, and (iii) the complex structure of the $|Bi_{1.5}Ba_{0.5}O_{2.25}|_\infty$ layers. In the latter layers barium and bismuth are located in two distinct (4*e*) sites, the majority of the oxygen atoms are located at the same level as bismuth, forming flat layers, and their positions correspond to a splitting with respect to the ideal one. The excess oxygen appears to be located between the double bismuth layers. The coordination of bismuth and barium is also discussed. © 1994 Academic Press, Inc.

INTRODUCTION

The layered bismuth cuprates $Bi_2Sr_2Ca_{m-1}Cu_mO_{2m+4+\delta}$ have been extensively studied over the last 5 years for their superconducting properties at high temperature. One important feature of these compounds is the modulation of their structure, which is at the present time a subject of controversy (for review see Ref (1)). It is indeed not yet known whether the incommensurability is due to the presence of excess oxygen in the bismuth bilayers or to the $6s^2$ lone pair of Bi (III).

This incommensurability of the structure makes difficult the location of oxygen in the bismuth layers, and also the determination of the cationic distribution in the distorted rock salt-type layers. In this respect the "2212"-type phase $Bi_{2-x}La_xBa_{2.5}La_{0.5}Cu_2O_{8.25}$ (2) is of great interest since it is the only bismuth-based layered cuprate that crystallizes in a tetragonal cell, with the *a* parameter close to that of the cubic perovskite and without any modulation of the structure. The preliminary powder X-ray diffraction study of this phase (2) did not permit the excess oxygen with respect to the "O_8" stoichiometry to be located and the oxygen positions to be determined accurately. Likewise, it was not possible to determine the distribution

of La^{3+} and Ba^{2+} cations owing to their isoelectronic configuration. In order to answer these questions we have investigated this phase by neutron diffraction. In the present paper we show that the crystal structure $Bi_{1.5}Ba_{2.5}LaCu_2O_{8.25}$ (the 2212 structure) accomodates excess oxygen without inducing any modulation.

EXPERIMENTAL

Sample Preparation

About 10 g of $Bi_{1.5}Ba_{2.5}LaCu_2O_{8.25}$ was synthesized in the following manner: Powders of Bi_2O_3, $Ba(NO_3)_2$, $La(NO_3)_3 \cdot 6H_2O$, and CuO, in the molar ratios 0.75/2.5/1/2, were thoroughly mixed in an agate mortar. The mixture was then heated at 800°C for 24 hr in argon flow and furnace cooled. After this thermal treatment, the powder was reground and pressed in the form of pellets of about 1 g each, and the thermal cycle was repeated. After synthesis, the pellets were reground and kept in dried air, owing to the sensitivity to air exposure, which leads to amorphization of the samples.

Neutron Diffraction

Powder neutron diffraction data were collected on the diffractometer DIA ($\lambda = 1.980$ Å), coming from the Institut Laue Langevin (Grenoble), which is installed in the guide G4.2 of the Laboratory Leon Brillouin (Saclay). We used an angular range $-6° \leq 2\theta \leq 145.5°$ in steps of $0.05°$ (2θ). After collection, a X-ray diffraction pattern was recorded in order to verify that the sample was not altered. The structure was studied using a Rietveld method (profile refinement computer program DBW 3.2 (3)). Scattering lengths were 0.8526, 0.8240, 0.7718, 0.5250, and 0.5805 (in 10^{-12} cm) for Bi, La, Cu, Ba, and O, respectively.

RESULTS AND DISCUSSION

The neutron diffraction pattern can be indexed in a tetragonal cell with parameters $a = 3.9322$ (1) and $c =$

TABLE 1
Refined Crystal Data for $Bi_{1.5}Ba_{2.5}LaCu_2O_{8.25}$

		Starting model							Refined model				
Atom	Site	x	y	z	B	τ	Atom	Site	x	y	z	B	τ
Bi	4e	1/2	1/2	0.2057	2.4	0.75	Bi	4e	1/2	1/2	0.2025(2)	1.6(1)	0.75
La(1)	4e	1/2	1/2	0.2057	2.4	0.25	Ba(1)	4e	1/2	1/2	0.2145(12)	1.6(1)[b]	0.25
Ba(1)	4e	0	0	0.1184	0.4	1	Ba(2)	4e	0	0	0.1180(1)	0.4(1)	1
Ba(2)	2a	0	0	0	2.0	0.5							
La(2)	2a	0	0	0	2.0	0.5	La	2a	0	0	0	1.3(1)	1
Cu	4e	1/2	1/2	0.0599	0.6	1	Cu	4e	1/2	1/2	0.0565(1)	1.0(1)	1
O(1)	8g	1/2	0	0.053	1.0	1	O(1)	8g	1/2	0	0.0509(1)	0.8(1)	1
O(2)	4e	0	0	0.197	1.0	1	O(2)	16n	0.173(2)	0	0.2036(3)	a	0.231(8)
O(3)	4e	1/2	1/2	0.136	1.0	1	O(3)	4e	1/2	1/2	0.1344(2)	1.5(1)	1
							O(4)	8g	1/2	0	0.278(1)	1.0	0.099(5)

$R_p = 8.55\%, R_{wp} = 13.14\%, R_i = 29.6\%, \chi^2 = 10.8$ $R_p = 3.47\%, R_{wp} = 4.36\%, R_i = 5.10\%, \chi^2 = 1.17$

[a] $\beta_{11} = 0.0198(117), \beta_{22} = 0.0416(118), \beta_{33} = 0.0017(2), \beta_{12} = 0, \beta_{13} = 0.0039(8), \beta_{23} = 0$.
[b] Fixed at the same value as B_{Bi}.

31.240(1) Å, except for some weak peaks which can be attributed to a $BaBiO_3$- type phase and to an unknown phase. Calculations were performed in the space group $I4/mmm$ using the data collected in the range $10° \leq 2\theta \leq 115°$; $BaBiO_3$ (4) was introduced as a secondary phase.

The starting model was that published in Ref. (2) from the X-ray diffraction study (see Table 1). For this model, the different R factors were $R_p = 8.55\%, R_{wp} = 13.14\%, R_i = 29.6\%$. Refinements of the positional parameters (z) and the B factor for all the atoms allowed these factors to be decreased to $R_p = 4.36\%, R_{wp} = 5.85\%, R_i = 9.94\%$, without any large variation of the z values but with spectacular variations for the isotropic thermal factors B for some atoms. The refined B values were 3.5, -1.2, and 26.6 Å² for (Bi, La(1)), (Ba(2), La(2)), and O(2), respectively. Considering the scattering lengths for barium and lanthanum, which are 0.5250 and 0.8240 10^{-12} cm, respectively, the negative B value obtained for barium and lanthanum located on the $(2a)$ site suggests that this site is mainly occupied by lanthanum instead of barium. This implies that barium should occupy the bismuth sites $(4c)$ instead of lanthanum. Such a distribution is consistent with the high B value observed for this site. To explain the abnormal high B value observed for O(2), a possible displacement of this atom from the position (0, 0, 0.2) was considered. To check this hypothesis, difference Fourier maps using calculated phases and amplitudes corresponding to $|F_o| - |F_c|$ values were performed after removing O(2) from the structure. Figure 1 shows a map calculated in the (ac) plane for $-0.5 \leq x \leq + 0.5, 0.1 \leq z \leq 0.4$, and $y = 0.0$. At the level of the O(2) position a residue is clearly visible; its shape suggests: (i) a splitting of the $(4e)$ sites (0, 0, 0.2) into the $(16n)$ sites $(x, 0, 0.2,$ with $x \approx 0.11)$, and (ii) an anisotropic thermal vibration. Moreover,

residues of smaller amplitudes at (1/2, 0, 0.22) and (1/2, 0, 0.28), suggesting a partial occupation of $(8g)$ sites, are also observed. Thus, new calculations were performed with mixed bismuth and barium in $(4e)$, lanthanum in $(2a)$, and O(2) in $(16n)$, with an occupancy factor $\tau = 0.25$ and anisotropic thermal factors. The refinements of the different variables led to $R_p = 3.71\%, R_{wp} = 4.64\%$, and $R_i = 6.7\%$, with $B_{Bi/Ba} = 2.3$ Å² and $B_{La} = 1.4$ Å², and for O(2) $x = 0.1993$ (3), $\beta_{11} = 0.3027, \beta_{22} = 0.0715, \beta_{33} = 0.0015, \beta_{13} = 0.0161, \beta_{12} = \beta_{23} = 0$. All calculations were performed without taking excess of oxygen in account, theoretically 0.25, in addition to 8. Considering the residues in the difference Fourier section at (1/2, 0, 0.22) and (1/2, 0, 0.28) (Fig. 1), supplementary oxygen O(4)
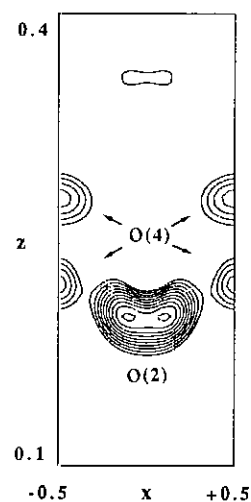

FIG. 1. Difference Fourier map section in the (ac) plane at $y = 0.0$ to locate O(2) and O(4) oxygen atoms.
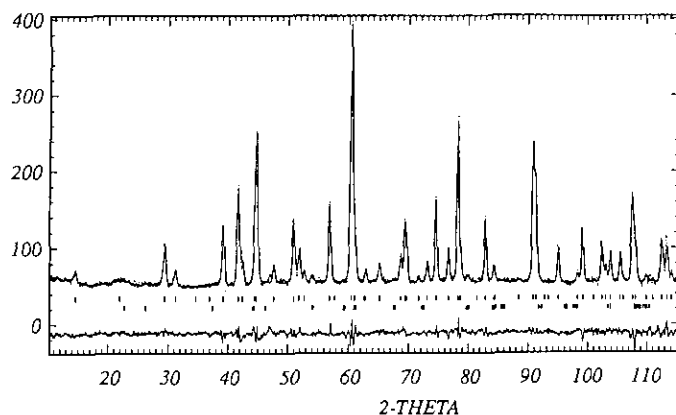
FIG. 2. Powder neutron diffraction patterns: experimental (dotted line), calculated and difference patterns (solid lines). The marks correspond to Bragg angle positions for $Bi_{1.5}Ba_{2.5}LaCu_2O_{8.25}$ (upper marks) and for $BaBiO_3$ (lower marks).

was introduced in $(8g)$ sites $(1/2, 0, z)$, with $z \approx 0.22$. Successive refinements of all positional variables, of thermal factors, of the occupancy factor of $O(4)$ sites, and then of $O(2)$ sites, reduced the R factors down to $R_p = 3.47\%$, $R_{wp} = 4.36\%$, $R_i = 5.20\%$. Note that owing to the low value obtained for the occupancy of $O(4)$ sites (about 10%), $B_{O(4)}$ was fixed at $1.0 \, \text{Å}^2$ during the calculations. The significant decrease of R_i from 6.6 to 5.2%, by introducing the $O(4)$ site, is in perfect agreement with the large decrease of β_{11} for $O(2)$ of about one order of magnitude. However, at this stage one problem still remained, namely the Ba–O(3) distance between barium located in the bismuth layers and the oxyen $O(3)$ at the apex of the CuO_5 pyramids. This abnormally short distance (2.19 Å) suggested that the additional barium was not located exactly on the same site as bismuth, but on a second $(4e)$ site at a different z level. This hypothesis did not lead to significant variations of the R factors but allowed a decrease in the B values for Bi and Ba from 2.3 to 1.6 Å^2. The final parameters are given in Table 1. Experimental, calculated, and difference diffraction patterns are plotted in Fig. 2. This study shows that this bismuth-based cuprate compound should be written $(Bi_{1.5}Ba_{0.5})Ba_2LaCu_2O_{8.25}$ instead of the formula $(Bi_{1.5}La_{0.5})Ba_2(Ba_{0.5}La_{0.5})Cu_2O_{8.25}$ previously mentioned (2). Note that the oxygen content deduced from the refinement "$O_{8.24}$" is very close to the theoretical value, $O_{8.25}$ deduced from the change balance. Note also that the lattice constants are greater than those of Bi_2Sr_2La $Cu_2O_{8+\delta}$ $(a/\sqrt{2} = 3.875 \, \text{Å}, c = 30.59 \, \text{Å})$ (5), in agreement with the relative size of Ba^{2+} and Sr^{2+}.

The analysis of these structural results allows the following features to be emphasized:

(i) The copper and oxygen atoms $O(1)$ forming the basal plane of the CuO_5 pyramids exhibit significantly different

z values (Table 1), so that copper is located inside the CuO_5 pyramids. Thus the $[CuO_2]_\infty$ layers are not flat, but puckered (Fig. 3), with $O(1)$–Cu–$O(1)$ and $O(1)$–Cu–$O(3)$ angles of 170° and 95° instead of 180° and 90°, respectively.

(ii) The fluorite-type cages, where the La^{+3} ions sit form a tetragonal prism with $O(1)$–$O(1)$ edges of 2.78 Å on the (a, b) plane and $O(1)$–$O(1)$ edges along c of 3.18 Å. These interlayer $O(1)$–$O(1)$ distances (Fig. 3) are larger than those of the NdO_8 cages (3.03 Å) in $Tl_2Ba_2NdCu_2O_{7-\delta}$ (6), in agreement with the relative sizes of La^{3+} and Nd^{3+}.

(iii) The Cu–Cu interlayer distances along c are high (3.53 Å) compared to those of the strontium homologue, which exhibits Cu–Cu distances ranging from 3.18 to 3.35 Å (7–13), and to those of the thallium superconducting cuprates for which values ranging from 3.16 to 3.34 Å are observed (6, 14–18). This feature may also be connected with the absence of superconductivity.

(iv) The Ba(2) and O(3) atoms exhibit different z coordinates (Table 1), so that the formed $[BaO]_x$ layers are also puckered (Fig. 4), the barium atoms being displaced toward the "O_1" layers, with respect to the apical oxygen $O(3)$. The corresponding Ba distances, as well as the apical Cu–$O(3)$ distance, are close to those usually observed (Table 2).

(v) The structure of the bilayer $[(Bi_{0.75}Ba_{0.25}O_{1.125})_2]_\infty$ is complex. The barium atoms Ba(1) located in these layers have a z coordinate larger than that of bismuth, i.e., they move toward the core of the bismuth bilayers (Fig. 4) in order to increase their distance to oxygen $O(3)$, which becomes 2.50 Å instead of 2.13 Å for the Bi–$O(3)$ distance (Table 2). The oxygen atoms $O(2)$ are located approximately at the same level as bismuth atoms (Fig. 4), but
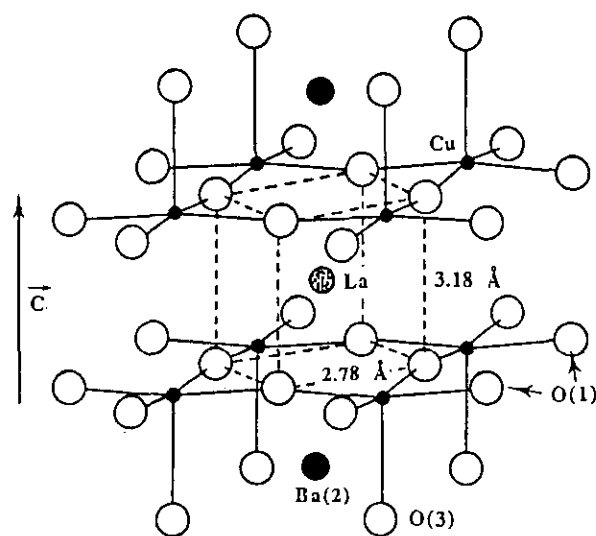

FIG. 3. Perspective view of the double perovskite layer showing the puckering of the $[CuO_2]_x$ sheets. A LaO_8 fluorite-type cage is indicated with dotted lines.

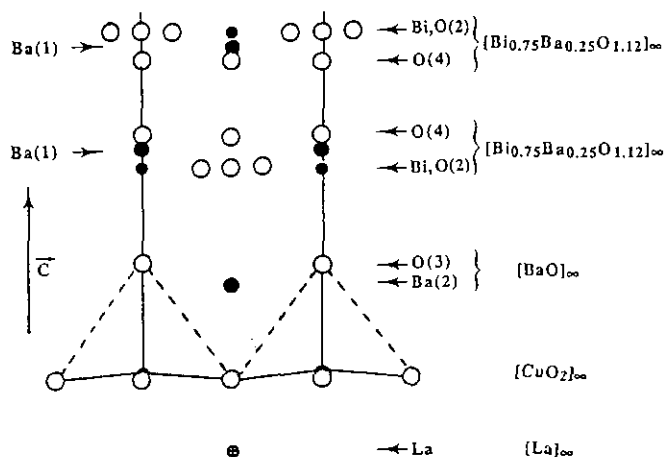FIG. 4. Partial schematic representation of the stacking of the different layers along c. In the $[Bi_{0.75}Ba_{0.25}O_{1.12}]_x$ layers, the Bi site is 75% filled, the Ba site is 25% filled, the O(2) site is 23% filled, and the O(4) site is 10% filled.

they are significantly removed from their ideal positions. The B values for O(2) are not very accurate; this suggests that two sets of oxygen atoms might exist, one surrounding bismuth and another one surrounding barium. Unfortunately, it was not possible to test this hypothesis, since this step increases the number of variable parameters. A slight oxygen deficiency was observed for these O(3) sites ($\tau = 0.231(8)$ instead of 0.25 for a full occupancy). Supplementary oxygen atoms O(4) were found. They are distributed over (8g) positions with an occupancy factor of about 0.1; the corresponding positions are located half-way between two bismuth (or barium) atoms along a and b, but at a different level, so that they are inside the "bismuth" bilayers (Fig. 4).

(vi) The coordinations of barium and bismuth in the mixed layers depend on their distribution with respect to each other and on the oxygen occupancy of the O(4) site.

TABLE 2
Interatomic Distances (in Å)

Bi–O(2)^a × 8	2.349(4)	Ba(1)–O(2)^a × 8	2.374(7)
Bi–O(2)^a × 8	3.297(7)	Ba(1)–O(2)^a × 8	3.314(8)
Bi–O(2)^b × 4	3.011(11)	Ba(1)–O(2)^b × 4	2.647(37)
Bi–O(3) × 1	2.127(9)	Ba(1)–O(3) × 1	2.502(38)
Bi–O(4)^a × 4	2.058(10)	Ba(1)–O(4)^a × 4	1.980(6)
Bi–O(4)^b × 4	3.071(27)	Ba(1)–O(4)^b × 4	2.793(36)
Ba(2)–O(1) × 4	2.874(3)	La–O(1) × 8	2.529(2)
Ba(2)–O(2) × 4	2.759(10)	Cu–O(1) × 4	1.974(0)
Ba(2)–O(3) × 4	2.827(1)	Cu–O(3) × 1	2.434(7)

^{a} In-plane distances.
^{b} Out-of-plane distances.
Note. To take into account of the occupancy factor of O(2) on (16n) sites, the number of neighboring O(2) must be divided by four.

Clearly the Ba(1)–O distances of 2.37 Å (Ba(1)–O(2)) and 1.98 Å (Ba(1)–O(4)) (Table 2) are not possible; they can easily be avoided since the Ba(1), O(2), and O(4) sites have a low occupancy factor of 25, 23, and 10%, respectively. As a result, Ba(1) may exhibit either a sixfold or a sevenfold coordination, according to whether or not one additional oxygen is present at the O(4) site. One indeed observes a distorted octahedron BaO_6 (Fig. 5a) with four oxygen atoms at 3.31 Å (O(2) in plane), one oxygen atom at 2.65 Å (O(2) out of plane), and one oxygen atom at 2.50 Å (O(3)); a monocapped octahedron can be formed (Fig. 5a) if one O(4) site at a distance of 2.79 Å is occupied. In the case of bismuth, one can consider the possibility that the oxygen atoms associated with Bi–O distances equal or larger than 3 Å do not participate in chemical bonding; then only three sets of Bi–O distances have to be considered (Table 2). We further have to take into consideration the ratio Bi/Ba = 3, which implies that a bismuth ion has two or three barium ions and four or five other bismuth ions as the nearest "in-plane" neighbors.
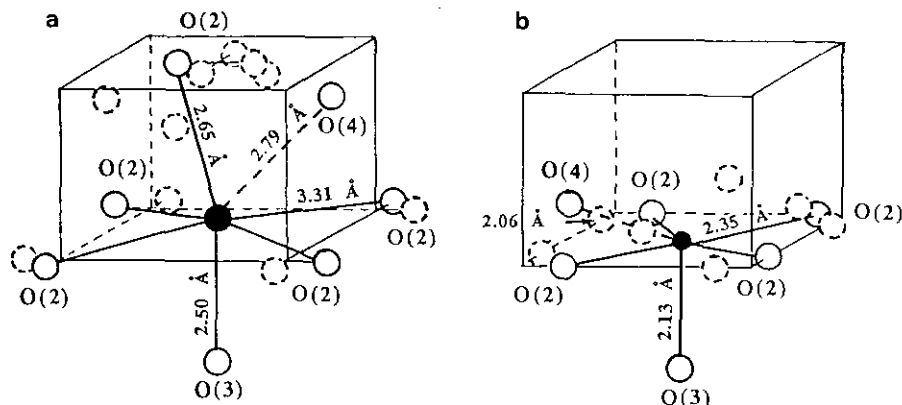

FIG. 5. Possible oxygen environment for Ba(2) (a) and Bi (b) in the $[Bi_{0.75}Ba_{0.25}O_{1.12}]_x$ layers. Only oxygen atoms at distances larger than 2.5 Å (a) and less than 2.5 Å (b) are represented. Some oxygen atoms are drawn with solid lines just as a guide for the eyes when several possiblities occur.

Moreover, when one barium and one bismuth atom are neighbors, the corresponding oxygen atoms O(2) have to move toward the bismuth site in order to avoid an abnormally short Ba–O (2) distance. As a result, one can assume that bismuth is on the average surrounded by four oxygen atoms O(2). Thus, bismuth can exhibit either a fivefold coordination with four oxygen atoms at 2.35 Å (O(2), and one at 2.13 Å, O(3)) or a sixfold coordination due to the presence of an additional oxygen on the O(4) site at a distance of 2.06 Å (Fig. 5b).

CONCLUSION

This structural study demonstrates that the introduction of excess oxygen does not necessary imply a modulation of the 2212 structure. It also shows for the first time that bismuth sites can be occupied by barium ions in spite of their larger size. These results support the viewpoint previously developed concerning the role of the $6s^2$ lone pair of Bi (III) in the incommensurability of these structures (19). In this phase, the absence of modulations can be explained by the fact that the barium cations significantly dilate the lattice, leaving enough room for the $6s^2$ lone pair of bismuth, thereby avoiding a distortion of the bismuth–oxygen layers.

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