JOURNAL OF SOLID STATE CHEMISTRY 119, 169–175 (1995)

New Shear-like Structure: The 2212-Related Cuprate $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$

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Received October 6, 1994; in revised form April 10, 1995; accepted April 17, 1995

The strategy of shearing mechanism has been applied to the 2212 bismuth cuprate $Bi_2Sr_2CaCu_2O_8$. A new compound has been synthesized, $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$; it crystallizes in a monoclinic cell with a = 48.40 (1) Å, b = 5.495 (1) Å, c = 16.283 (4) Å, and β = 109.96 (2)°. This phase exhibits 2212 ribbons running along c that are 9 Bi atoms wide, and shifted by 5.3 Å with respect to each other; these ribbons are interconnected through thin layers involving CuO_6 octahedra. In spite of its close relations with an ideal (101)-shear "2212" structure, this cuprate cannot be considered as such and is termed (101)-collapsed "2212" cuprate in agreement with previous works on (010)-collapsed "2201" cuprates. The rupture of the $[CuO_2]_\infty$ layers and the possibility of using these phenomena for creating columnar defects in high-T_c superconducting cuprates are also discussed. © 1995 Academic Press, Inc.

INTRODUCTION

The layered cuprates, $(AO)_n^{RS}$ $(A'CuO_{3-x})_m$, form a large family whose superconducting properties are due to the presence of infinite $[CuO_2]_\infty$ layers [see for review Ref. (1)]. The shearing phenomena that may take place transversally to these layers are of high importance for the existence of superconductivity, since they can lead to the rupture of the $[CuO_2]_\infty$ layers and consequently to a disappearance of superconductivity. This is the case of the bismuth cuprates $Bi_{17}Sr_{16}Cu_7O_{49}$ (2), $Bi_{14+x}Sr_7Ba_7Cu_{7-x}O_{42+x/2}$ (3), and $Bi_6Ba_4Cu_2O_{15}$ (4), which do not superconduct, apparently because of the absence of infinite copper layers. These compounds, which have been termed "collapsed cuprates," derive from the 2201 phase $Bi_2Sr_2CuO_6$ (Refs. (5, 6) and Fig. 1a) forming "2201" ribbons with various thicknesses. The two first compounds can be considered as n = 8 and 7 members of the series $(Bi_2A_2CuO_6)_{n-2}(Bi_{4+x}A_4Cu_{2-x}O_{12+x/2})$; they are in fact shear structures derived from "2201," with a $(010)_{2201}$ shear plane as shown, for instance, for the n = 8 member, which exhibits 2201-type ribbons that are eight octahedra wide (Fig. 1b). The third compound $Bi_6Ba_4Cu_2O_{15}$, termed double-collapsed "2201" structure, consists of ribbons of the "2201" structure that are five octahedra wide parallel to $(012)_{2201}$ (Fig. 1c). Although it looks like a shear structure, this phase cannot be described as a true one, since two successive "2201" ribbons are not related to each other through a $(102)_{2201}$ crystallographic shear plane; nevertheless, there exist disconnected shearing operations (translations along **c** and **a** that allow the "2201" structure to be reconstructed.

It is essential to understand these shearing mechanisms to be able to generate new cuprates, superconducting or not. The possibility to realize shearing phenomena in the bismuth "2212" cuprate has not yet been investigated up to date for the creation of new collapsed bismuth phases. This paper is devoted to the exploration of such compounds. It deals with the synthesis and characterisation of a new phase, $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$, that corresponds to a collapsed "2212" cuprate by a shearing mechanism.

Strategy of the Synthesis

Considering the formula of the collapsed bismuth cuprates previously synthesized, it appears that such structures are stabilized by a "partial substitution" of bismuth or strontium for copper with respect to the ideal parent cuprates. One can indeed notice that the three collapsed "2201" phases (2–4) have a chemical formula close to that of "$Bi_2Sr_2CuO_6$" and can be expressed "$Bi_{2+x}Sr_{2+y}Cu_{1-z}O_{6+t}$."

In order to generate new collapsed phases, this "partial substitution" was applied to the ideal formula of the hypothetical calcium free "2212" phase, i.e.," $Bi_2Sr_3Cu_2O_8$." In this way, a series of chemical formulations was investigated, $Bi_{2+x}Sr_{3+y}Cu_{2-z}O_{8+t}$, x, y, and z were systematically varied by steps of 0.1, with x, y, z ranging from 0 to 1.

The samples were synthesized from mixtures of Bi_2O_3, $SrCO_3$, and CuO, pressed in the form of bars, and heated at 800°C in an oxygen flow for 48 to 65 h. The best result was obtained for the nominal composition $Bi_{1.8}Sr_{3.3}Cu_{2.0}O_{8+t}$. Nevertheless, traces of $Sr_{14}Cu_{24}O_{41}$ and of the collapsed "2201" cuprate, $Bi_{17}Sr_{16}Cu_7O_{49}$, were always detected whatever the thermal treatment.

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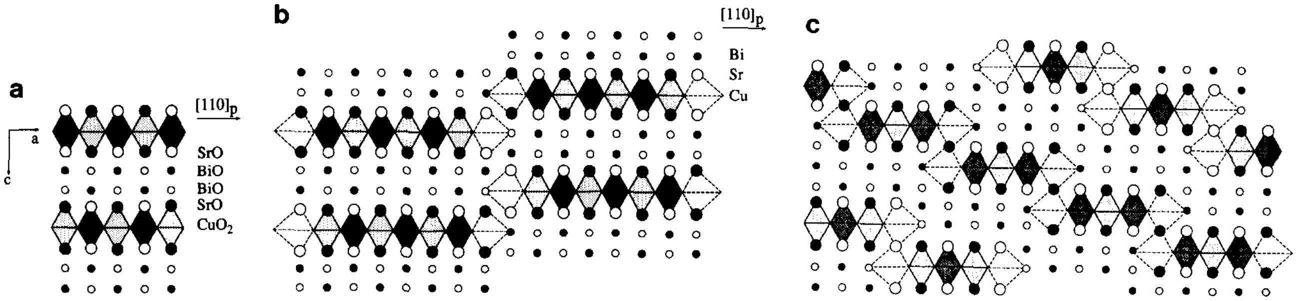

FIG. 1. Idealized drawings of (a) "2201" structure, $Bi_2Sr_2CuO_6$; (b) "2201" collapsed structure, $n = 8$, $Bi_{17}Sr_{16}Cu_7O_{49}$; and (c) "2201" double-collapsed structure, $n = 5$, $Bi_6Ba_4Cu_2O_{15}$. These structures are projected along the $[110]_p$ direction of the perovskite. The nature and the environment of the cations located at the level of the crystallographic collapsing plane (dotted lines) are not well defined.

X-Ray Diffraction and Electron Diffraction Characterization

The X-ray powder diffraction (XRD) was performed with a PHILIPS vertical goniometer, using Cu $K\alpha$ radiation in the range $3° \leq 2\theta \leq 70°$ by step scanning with an increment of 0.02° (2θ). Lattice constants were determined using the profile refinement computer program FULLPROF (7). Electron diffraction (ED) was carried out with a JEOL 200 CX electron microscope. EDX analyses were systematically performed on numerous crystals of the different samples, with a KEVEX analyzer.

The EDX analyses, performed on about 30 crystals, allowed the nominal cationic composition to be confirmed, i.e., $Bi_{1.8}Sr_{3.3}Cu_2$. Taking into account the EDX and structural results that will be developed further, the collapsed "2212" cuprate will be formulated $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$ (instead of $Bi_{1.8}Sr_{3.3}Cu_2O_{8+t}$).

The reconstruction of the reciprocal space evidences, in these compounds, a monoclinic symmetry; the [010] ED pattern is given in Fig. 2. Note that some crystals

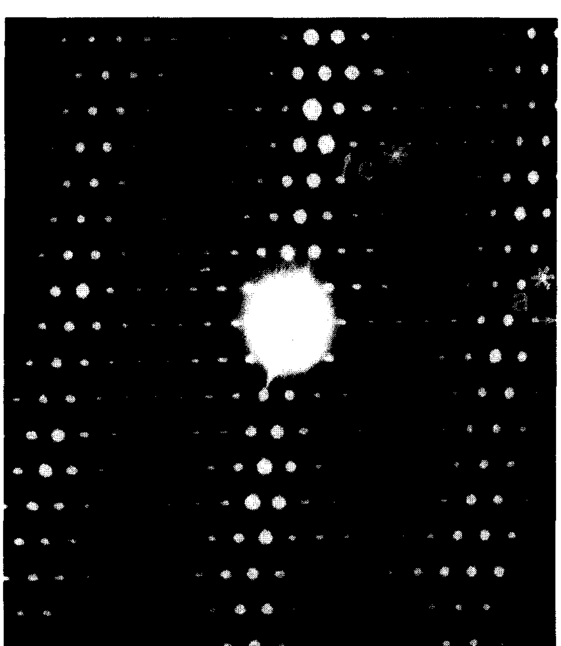

FIG. 2. [010] ED pattern of $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$.

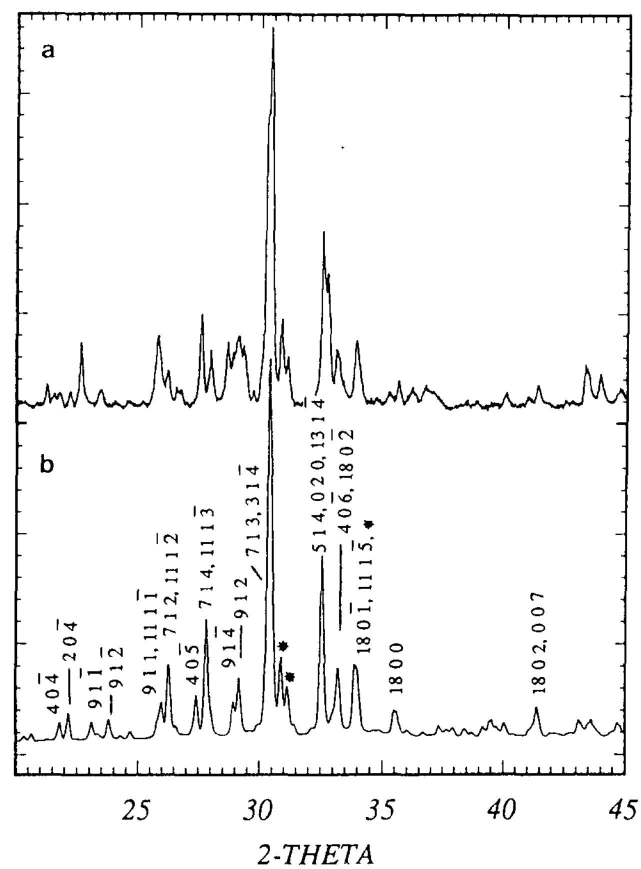

FIG. 3. X-ray powder diffraction patterns of $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$: (a) experimental pattern and (b) theoretical pattern calculated on the basis of the cationic positions deduced from HREM images. Peaks marked by asterisks are attributed to $Sr_{14}Cu_{24}O_{41}$.

of the collapsed cuprate $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$ exhibit streaks along a^* which have been correlated to the existence of local intergrowth defects.

On this basis, the cell parameters of these compounds were refined from the powder XRD patterns (Fig. 3) to the following values: a = 48.40(1)Å, b = 5.495(1)Å, c = 16.283(4)Å, and β = 109.962)° for $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta\omega}$ with hkl, $h + k = 2n$, involving the possible space groups $C2/m$, Cm, and $C2$.

High-Resolution Electron Microscopy Study

The great similarity between the [010] ED patterns of this phase and those of the 2201-collapsed cuprates (2–4) and the values of the cell parameters are strongly in favor of a shearing phenomenon. In order to confirm this hypothesis and to propose a structural model, a HREM study was performed with a TOPCON electron microscope operating at 200 kV and having a point resolution of 1.8 Å.

The [010] orientation, which allows the superstructure along **a** to be understood was chosen for the study. The interpretation of the experimental images was carried out by comparing images recorded for the "2201" and "2212" modulated phases (8–11) and the 2201-collapsed and double-collapsed phases (2–4).

The close relationships between the 2212-type structure of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and that of the new phase, $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$, can be easily evidenced by comparing the [010] HREM images of the two compounds (Refs. (8–11) and Fig. 4a). Two striking features appear clearly on the [010] images: first, the formation of ribbons parallel to **c**, i.e., to $[\bar{1}01]_{2212}$ and, second, the nature of the tapes, parallel to $(001)_{2212}$, which are stacked to constitute these ribbons. This is illustrated in Fig. 4a. One can identify the $[BiO]_\infty$ tapes; they are imaged as oval-shaped arrangements

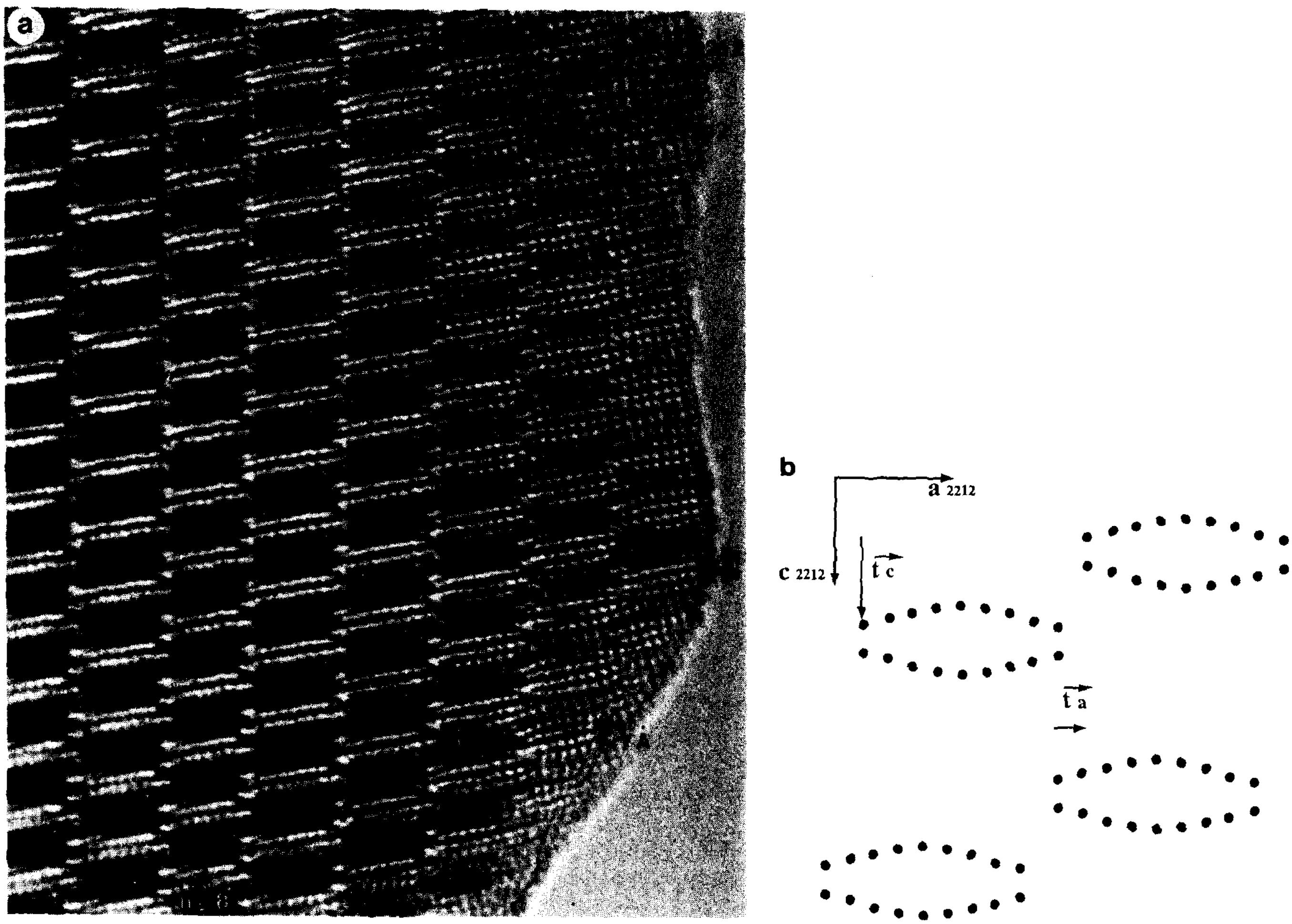

FIG. 4. $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$: (a) [010] high-resolution image, where the atoms are imaged as bright dots; the nature of the different layers is indicated as well as the a and c parameters of the "2212" parent structure. (b) Schematical representation of the relative arrangements of the oval-shaped bismuth segments.

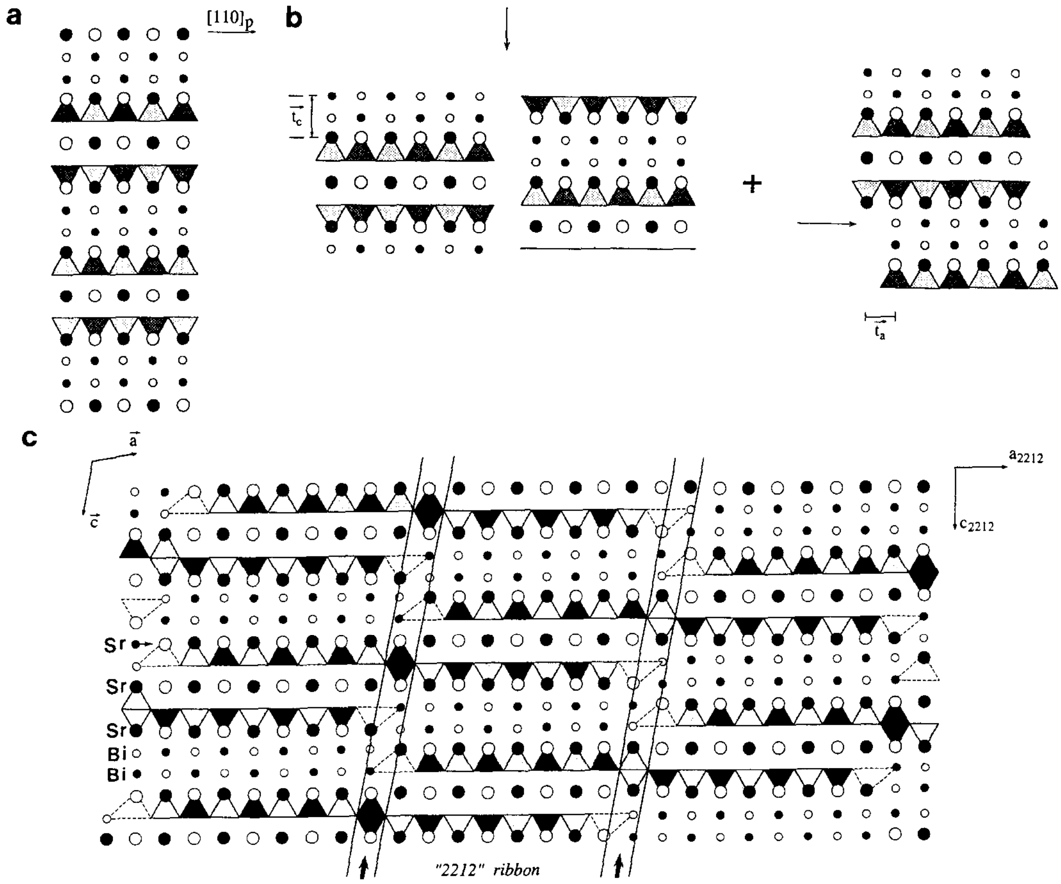

FIG. 5. Idealized drawings of (a) the "2212" parent structure projected along $[1\bar{1}0]_p$; (b) the two shiftings ($\mathbf{t}_c$ and $\mathbf{t}_a$), showing the involved junction of different layers; and (c) "2212" collapsed structure, $n = 9$, $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$.

formed by two segments of brightest spots running along $\mathbf{a}_{2212}$ (see indications in Fig. 4a). Above and below, two other rows of bright spots are observed which are attributed to the $[SrO]_\infty$ tapes. These units "SrO–BiO–BiO–SrO" are separated by one row of bright spots sandwiched between two rows of grey spots correlated to the copper layers, according to the sequence "CuO_2–SrO–CuO_2." This mode of layer stacking, observed right across a ribbon running along **c**, is consistent with a "2212"-type structure (Refs (12, 13) and Fig. 5a).

The oval shaped "Bi" segments are 24.5 Å wide, i.e., they correspond to nine adjacent Bi atoms. Two superposed oval-shaped segments in one ribbon are translated by $\mathbf{t}_a = 2.7$ Å ($a_p\sqrt{2}/2$) along $\mathbf{a}_{2212}$ and two ribbons are translated by $\mathbf{t}_c = 5.3$ Å with respect to each other. The relative arrangements of these bismuth ribbons with the corresponding translations are illustrated schematically in Fig. 5b. Such a shifting involves the junction of layers of different natures along the a_{2212} axis; to understand the mode of connection of the layers, a structural model, based on an undistorted 2212 framework (Fig. 5a), is shown in Fig. 5c. The idealized structure is built up from 2212 ribbons, running along **c**, that are eight CuO_5 pyramids thick; they are interconnected through one CuO_6 octahedron and distorted CuO_5 (or BiO_5) trigonal pyramids. At first sight, such a structure looks like a shear "2212" structure (that would be characterized by a (100) [or $(101)_{2212}$] crystallographic shear plane (*CSP*); in fact, the *CSP*s are replaced by a thin layer involving CuO_6 octahedra (see large arrows in Fig. 5c). Nevertheless, if one deletes these thin layers that form the boundary between two successive "2212" ribbons, the latter correspond to each other through a translation of about 5.3 Å. Thus, the collapsed cuprate $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$ is derived from the "2212" structure and characterized by the existence of $(101)_{2212}$ *CSP*s and a translation of 5.3 Å by introducing single layers, one octahedron thick, at the level of each shear plane.

The ideal formulation is $Bi_{18}Sr_{26}Cu_{17}O_{70}$, which is close to the nominal composition. However, this idealised model must, in fact, be corrected considering the experimental images:

(i) The oval shape of the segments results from the undulation of the $[BiO]_\infty$ tapes according to a movement

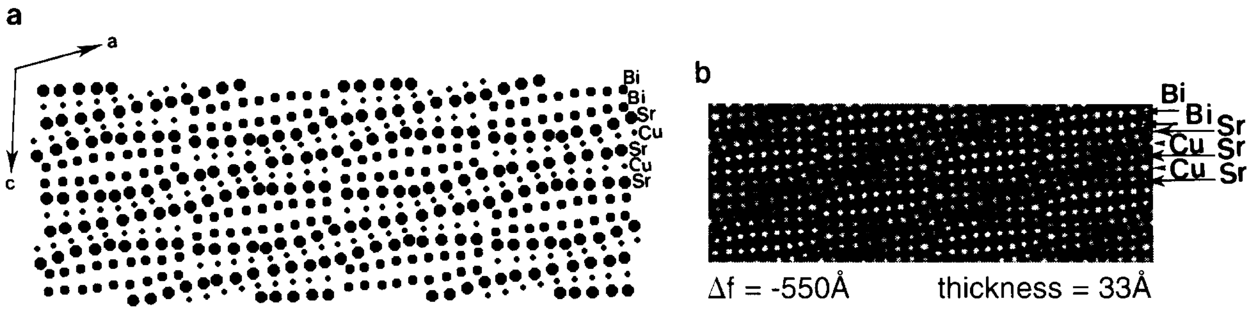

FIG. 6. (a) [010] projection of the model; (b) corresponding calculated image for $\Delta f = -55$ nm and crystal thickness of 3.3 nm.

similar to that observed in the "2212"-modulated superconductor and the collapsed "2201" phases. Since they suffer this modulation and because they are connected to layers which exhibit different thicknesses, the other layers (strontium and copper layers) also undulate in the matrix.

(ii) At the level of the connection of the different $(001)_{2212}$ tapes, contrast variations suggest cationic substitutions similar to those previously mentioned (2–4), especially at the junction between "Cu" and "Bi" segments; the nature and environment of the cation located at this level is not well defined (it is drawn in dashed lines in Fig. 5c). The disturbance observed at this level would explain the difference between the actual and theoretical compositions: $Bi_{16}/Sr_{28}/Cu_{17}$ instead of $Bi_{18}/Sr_{26}/Cu_{17}$.

The thermogravimetric analysis, performed at 480°C under Ar/H_2 flow for 14 hr, evidences an oxygen excess $\delta \approx 2$. This oxygen could be located either in the BiO layers, as observed in the $Bi_2Sr_2LnCu_2O_{8+\delta}$ cuprates (14), or at the level of the Sr atoms located between the two copper segments. In any case, this implies that copper is mainly in pyramidal coordination. This result is, moreover, in agreement with the HREM images where the estimated Cu–Cu distances are close to 3.7 Å and correspond to that obtained in $La_2SrCu_2O_6$ (15), 3.66 Å, where similar perovskite slices are observed, with Sr atoms in eightfold coordination located between two pyramidal copper layers.

Image calculations (Fig. 6) performed with ideal positional parameters deduced from the 2212 structure (Table 1) taking the layer undulations into account (Fig. 6a) confirm the structural model. The weak streaks observed along a^* arise from the existence of defective n members; an example is shown in Fig. 4a, where a ribbon $n = 8$ is indicated by a curved arrow.

Owing to the complexity of the structure, and especially to the large cell parameters, structure refinements, have not been carried out from X-ray powder data. The very large number of independent atoms (31 independent metallic atoms, i.e., 62 variable parameters for the cationic positions only) does not allow a structural calculation to be made. Nevertheless, the profile of the XRD pattern calculated from the ideal positions (Fig. 3b) is not too far from the experimental pattern (Fig. 3a), taking into account the fact that the oxygen positions cannot be seriously introduced in the calculation and that orientation phenomena, observed in most of the bismuth cuprates due to the lamellar character of the structures, are also not considered.

DISCUSSION

The cuprate $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$ represents an original collapsed structure that is deduced from the layered "2212" cuprates by applying a shearing mechanism. The collapsed copper-based phases that have been synthesized up to date are listed in Table 2, together with their mother structures. Among these four compounds, $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$ is the only one that involves CuO_5 pyramids, the others being built up from CuO_6 octahedra.

The first important observation deals with the fact that

TABLE 1
Cationic Positions Deduced from HREM Images and Used for Image Calculations (Space Group $C2$)

Cation	x/a	y/b	z/c	Cation	x/a	y/b	z/c
Bi(1)	0.0308	0.5	0.9338	Cu(8)	0.4440	0.0	0.4752
Bi(2)	0.0880	0.0	0.9700	Cu(9)	0.5000	0.5	0.5000
Bi(3)	0.0358	0.0	0.7749	Sr(1)	0.0352	0.0	0.0647
Bi(4)	0.0891	0.5	0.8094	Sr(2)	0.0897	0.5	0.1229
Bi(5)	0.1400	0.0	0.8301	Sr(3)	0.1530	0.0	0.1762
Bi(6)	0.1963	0.5	0.8600	Sr(4)	0.2132	0.5	0.2286
Bi(7)	0.2500	0.0	0.9041	Sr(5)	0.2608	0.0	0.2854
Bi(8)	0.3058	0.5	0.9381	Sr(6)	0.3106	0.5	0.3001
Bi(9)	0.3568	0.0	0.9745	Sr(7)	0.3715	0.0	0.3448
Cu(1)	0.0358	0.5	0.2178	Sr(8)	0.4298	0.5	0.3520
Cu(2)	0.0977	0.0	0.2643	Sr(9)	0.4899	0.0	0.3516
Cu(3)	0.1523	0.5	0.3034	Sr(10)	0.0450	0.0	0.3854
Cu(4)	0.2116	0.0	0.3509	Sr(11)	0.0923	0.5	0.4038
Cu(5)	0.2722	0.5	0.3960	Sr(12)	0.1576	0.0	0.4541
Cu(6)	0.3256	0.0	0.4268	Sr(13)	0.2148	0.5	0.4808
Cu(7)	0.3862	0.5	0.4582				

shearing mechanisms applied to the bismuth cuprates lead systematically to a rupture of the $[CuO_2]_\infty$ layers so that disappearance of superconductivity should be expected. This view point is confirmed by electrical measurements performed by the four-probe method on $Bi_{16}Sr_{28}Cu_{17}O_{69+\delta}$; a semiconducting behavior is indeed evidenced whatever the thermal annealing under argon, air, or oxygen at low temperature. Thus the collapsed bismuth cuprates do not superconduct (Table 2).

A second important feature concerns the width of the copper tapes running along [010] of this new shear-like structure. The octahedral or pyramidal copper tapes and their relative positions are represented in Fig. 7 without any drawing of the other cations. It appears clearly that the width of these tapes which corresponds to 17 CuO_5 pyramids for the collapsed 2212 cuprate (≈46 Å) is significantly larger than those observed for the collapsed 2201 cuprates that range from five octahedra (≈ 13.5 Å) to eight octahedra (≈21.6 Å). In this respect, this new structure is intermediate between the nonsuperconducting collapsed "2201" cuprates and the superconducting "2201" (5, 6) and "2212" (12, 13) cuprates which exhibit infinite copper layers instead of tapes. This interruption of the copper layers has very interesting potential applications for increasing the critical currents of the superconducting cuprates; attempts will be made to use this property to create chemical columnar defects of this collapsed nonsuperconducting structure grown coherently in a matrix of the superconducting mother matrix, in order to pin the vortices.

A third interesting characteristic of these collapsed phases deals with the oval-shaped segments observed in all the bismuth compounds. This property may be correlated to the stereoactivity of the $6s^2$ lone pair of Bi (III), which controls the undulation of the bismuth–oxygen layers in the mother structures. This suggests that the width of the ribbons not only is determined by the copper substitution, but may also be correlated to the amplitude of the undulation. One indeed observes that the width of the ribbons in the collapsed 2212 structure is "$9 \times a_p \sqrt{2}/2$," i.e., close to the modulation vector, $q = 9.3$, observed for the mother "2212" cuprate $Bi_2Sr_{3-x}Ca_xCu_2O_8$ prepared in the same conditions in an oxygen flow (16).

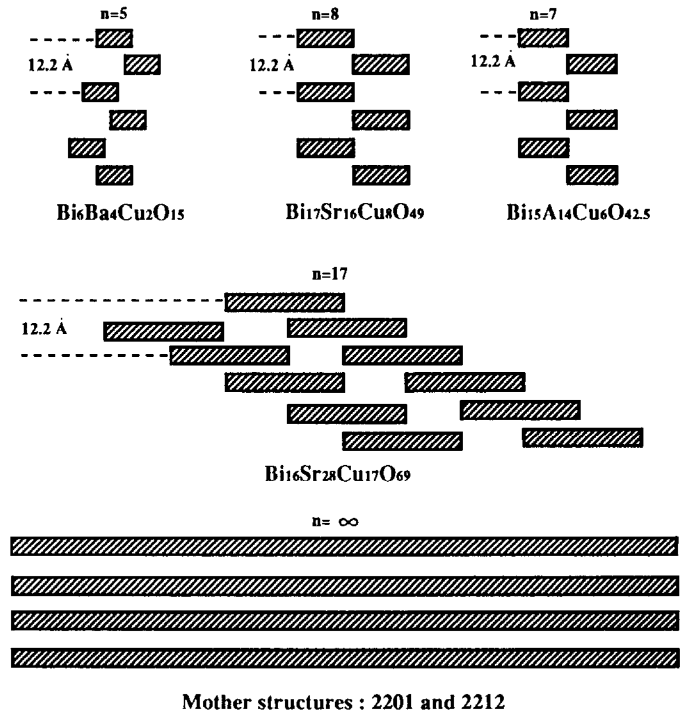

FIG. 7. Schematical representation of the different collapsed bismuth copper cuprates and parent structures. The hatched rectangles represent the copper tapes, whose lengths are proportional to the number of copper–oxygen polyhedra.

TABLE 2
Synthesized Copper Compounds

	Parent structure	Copper ribbon width	CCP	Ref.	T_c
Collapsed structures					
$Bi_{17}Sr_{16}Cu_7O_{49\pm\delta}$	2201	8	$\{100\}_{2201}$	(2)	NS
$Bi_{15}Ba_7Sr_{27}Cu_6O_{12\pm\delta}$	2201	7	$\{100\}_{2201}$	(3)	NS
$Bi_6Ba_4Cu_2O_{15\pm\delta}$	2201	5	$\{102\}_{2201}$	(4)	NS
$Bi_{16}Sr_{28}Cu_{17}O_{69\pm\delta}$	2212	17	$\{101\}_{2212}$	This work	NS
Parent structures					
"2201" $Bi_2Sr_2CuO_6$		∞	None	(5, 6)	22K
"2212" $Bi_2Sr_{3-x}Ca_xCu_2O_8$		∞	None	(12, 13)	94K

Finally, it must be emphasized that the stabilization of such a collapsed phase requires a copper deficiency with respect to the ideal formula of the corresponding high-T_c superconductors, as pointed out in the strategy of the synthesis of these materials. Nevertheless, the clue for the systematic synthesis of all the members of this family of cuprates, collapsed or not, is so far not yet found out as shown, for instance, for the only synthesis of the "2212" cuprate, which can be obtained only for the formulations $Bi_2Sr_{3-x}Ca_xCu_2O_8$ with $x \geq 0.4$, the composition $Bi_2Sr_3Cu_2O_8$ leading to a tubular phase (17) closely related to the 2201 bismuth cuprate. A systematic investigation will be needed to control the possible creation of collapsed-phase defects in a matrix of high-T_c superconducting cuprates or oxycarbonate.

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