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Tubular Bismuth Cuprates, a Large Family $(Bi_{2+x}Sr_{2-x}CuO_{6+\delta})_n(Sr_{8-x'}Cu_6O_{16+y})$ Closely Related to the 2201-Superconductor: An Electron Microscopy Study

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A new family of bismuth–copper oxides has been characterized by X-ray and electron diffraction techniques. Its structure is built up from the intergrowth, along the $\vec{b}$ axis, of n "2201"-type slices with a perovskite-related slice; the general formulation is $(Bi_{2+x}Sr_{2-x}CuO_6)_n(Sr_{8-x'}Cu_6O_{16+y})$. Four members were isolated, corresponding to $n = 4, 5, 6$, and 7; $n < 4$ and $n > 7$ members were only observed in an extended defect area. © 1992 Academic Press, Inc.

Introduction

Recently, a new tubular phase, $Bi_4Sr_8Cu_5O_{19+x}$ related to the superconducting perovskite intergrowths, was isolated and characterized by one of us (*1, 2*). The structure of this new oxide was described as a stacking of infinite rectangular tubes along the $\vec{a}$ axis of the orthorhombic cell, these tubes being constituted by a core of four parallel double "BiO" rows wrapped in a surface of a Sr–Cu–O perovskite layer. Moreover the authors emphasized the interesting structural relationships between this phase and the high T_c superconductor $Bi_2Sr_2CuO_6$ (*3, 4*), showing the breaking of the two-dimensionality of the 2201 structure by means of perovskite planes stacked perpendicularly to the $[CuO_2]_\infty$ layers. This study suggests the possibility to generate new phases intermediate between $Bi_2Sr_2CuO_6$ and $Bi_4Sr_8Cu_5O_{19+x}$. The present paper deals with the analysis of the structural mechanisms which govern the formation of new members with a tubular structure and their investigation by high resolution electron microscopy.

Structural Analysis: Prevision of a Large Family of Tubular Oxides $(Bi_{2+x}Sr_{2-x}CuO_{6+\delta})_n(Sr_{8-x'}Cu_6O_{16+y})$

In order to understand the structural relationships between 2201 phase and the tubular structure $Bi_4Sr_8Cu_5O_{19+x}$, one has to consider the view of the perovskite structure along the ⟨110⟩ direction of the perovskite cell (Fig. 1a). The well-known structure of the 2201-superconductor $Bi_2Sr_2CuO_6$ (Fig. 1b) consists of single perovskite layers $[SrCuO_3]_\infty$ intergrown with triple rock-salt layers $[Bi_2SrO_3]_\infty$. At this

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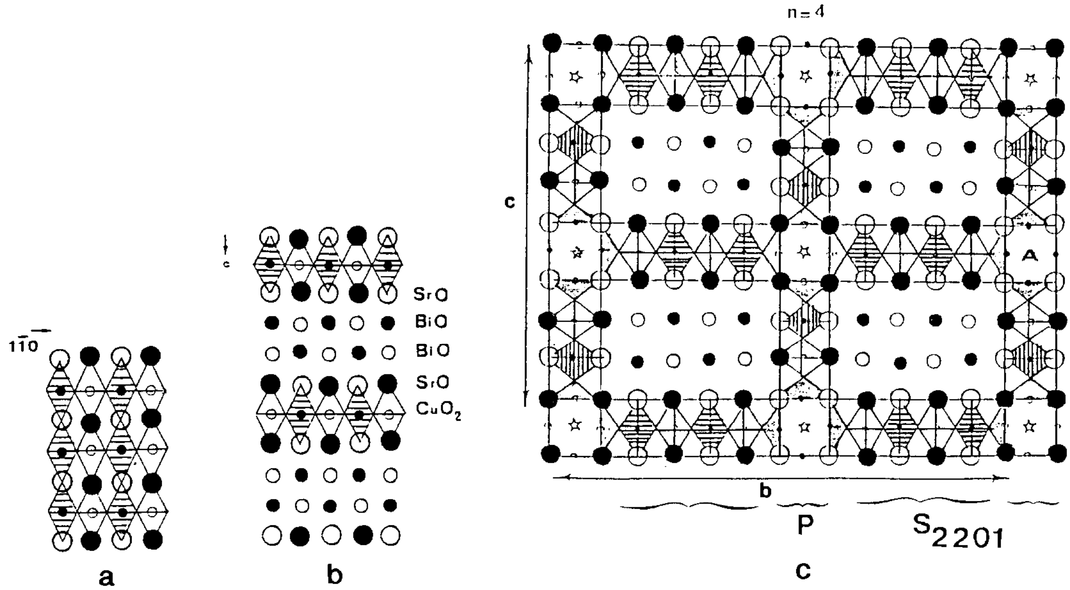

FIG. 1. Idealized projections of (a) the perovskite structure along the ⟨110⟩ direction; (b) the 2201 superconductor structure along ⟨100⟩, i.e., along ⟨110⟩p (p refers to the ideal perovskite cell); and (c) $Bi_4Sr_8Cu_5O_{19}$ along ⟨100⟩, i.e., along ⟨110⟩p (the star in the site labeled A corresponds to a highly disordered O; the site may be partially vacant).

stage of the structural representation it is worth pointing out that the $[SrO]_\infty$ or $[BiO]_\infty$ rows are parallel to $[110]_p$ and, consequently, oxygen and strontium or bismuth are projected on the same point on the schematized projection. The schematized projection of the tubular oxide $Bi_4Sr_8Cu_5O_{19+x}$ (Fig. 1c) shows its great similarity with the 2201 structure. One recognizes the existence of 2201-type slices parallel to (010), which are four CuO_6 octahedra wide along $\vec{b}$ i.e., involving four $[BiO]_\infty$ double rows running along $\vec{a}$ (labeled S_{2201}). Such slices which contain four copper octahedra can be formulated $[(Bi_2Sr_2CuO_6)_4]_\infty$. On both sides of each slice along $\vec{b}$, the propagation of the $[CuO_2]_\infty$ octahedral plane is interrupted by elimination of one out of two oxygens in a row along $\vec{a}$, leading to the formation of CuO_5 distorted trigonal bipyramids. In the same way, the propagation of the $[BiO]_\infty$ layers in the (001) plane is interrupted by replacement of bismuth by strontium and copper successively. It results in the formation of pillars (labeled P in Fig. 1c), characterized by the existence of cycles of four edge-sharing CuO_5 polyhedra; along $\vec{b}$ such cycles are connected through rows of four CuO_6 octahedra belonging to the $[(Bi_2Sr_2CuO_6)_4]$ slices, whereas along $\vec{c}$, they are connected through rows of two CuO_6 octahedra. These pillars which can be formulated $[Sr_8Cu_6O_{16}]_\infty$ can be described as related to the oxygen-deficient perovskite with a_p width along $\vec{b}$.

It must be noted that the oxygen atom on site A (stars) in the pillars is in fact highly disordered between two positions along the a axis (*2*). This site may be partially occupied, so that CuO_5 bipyramids may be partially replaced by CuO_4 tetrahedra.

Thus the structure of the tubular phase $Bi_4Sr_8Cu_5O_{19+x}$ can be described as an assemblage of quadruple 2201-type slices $[(Bi_2Sr_2CuO_6)_4]_\infty$ and of $[Sr_8Cu_6O_{16}]_\infty$-related perovskite pillars. Such a view of the structure suggests the existence of a new family, by variation of the thickness of the 2201 slice, i.e., by changing the number of CuO_6 octahedra along $\vec{b}$, leading to the formation of $[(Bi_2Sr_2CuO_6)_n]_\infty$ slices where $n = 2, 3,$ and 4. . . . In fact, the results obtained for the 2201 phase (*5–7*) and from neutron diffraction for $Bi_4Sr_8Cu_5O_{19}$ (*2*) suggest the existence of a strontium deficiency and bismuth excess. Thus a general formulation $(Bi_{2+x}Sr_{2-x}CuO_{6+\delta})_n(Sr_{8-x'}Cu_6O_{16+y})$ can be proposed for such a structural family, the tubular oxide $Bi_4Sr_8Cu_5O_{19+x}$ corresponding to the member $n = 4$.

Experimental

Considering the general formation of the new family, numerous compositions were tested for members $n = 2$ to 10, n being an integer or not, varying the cation's content close to an ideal formulation, temperatures (ranging from 750 to 880°C), atmosphere (air and nitrogen flows), and annealing times (from 24 hr to 15 days). Two ways of synthesis were adopted: either from the mixtures of Bi_2O_3, $SrCO_3$, and CuO in adequate molar ratios or from the mixtures of 2201 as a precursor with Sr_2CuO_3 and CuO (*2*).

Samples were systematically characterized by powder X-ray diffraction (Philips diffractometer using Cu$K\alpha$) and electron microscopy. The electron microscopy study was performed with a JEOL 120 CX microscope fitted with a side entry goniometer (±60°C) and a JEOL 200 CX electron microscope fitted with a double tilt goniometer (±10°C).

Results

Research of New Members

The first investigation of the Bi–Sr–Cu–O system was carried out following the mentioned experimental conditions, for n ranging from 2 to 10. The corresponding ideal compositions are given in Table I. The X-ray and electron diffraction studies of the numerous synthesized compounds allow some general remarks to be made:

—The members $n = 4$, 5, 6, and 7 are synthesized as "pure" or majority phases in air flow; the compositions and thermal treatments are given in Table I. It should be noted that even in the phases considered pure from X-ray diffraction some crystals of the 2201 oxide or of members with values different from the n expected value are always observed by E.D.

—No tubular phases have been synthesized when working in nitrogen flow; X-ray and electron diffraction give evidence of the formation of the monoclinic $Bi_{17}Sr_{16}Cu_7O_x$ collapsed phase (*8*).

—The temperature of synthesis influences considerably the stabilization of the different members. High temperatures, i.e., 880°C, favor the formation of the tubular-4 members.

—$n = 5$ and $n = 6$ members are difficult to stabilize, a mixture of $n = 4$ and $n = 7$ being easily obtained.

—An excess of strontium with regard to the ideal composition favors the formation of the monoclinic collapsed 2201 phase (*8*).

—All our attempts to synthesize new oxides corresponding to lower n values ($n \geq 8$) failed up to now.

The New Tubular Oxides n = 4, 5, 6, and 7

The first feature revealed by electron diffraction deals with the morphology of the crystals. A mica-like morphology is very quickly observed when n increases. No preferential orientation is indeed observed for the tubular-4 oxide, whereas the lamellar character of the tubular-7 is as strongly pronounced as that in the 2201 phase. The typical [001] electron diffrac-

TABLE I

IDEAL COMPOSITION OF THE $(Bi_{2+x}Sr_{2-x}CuO_6)_n$ $Sr_{8-x'}Cu_6O_{16+y}$ MEMBERS, EXPERIMENTAL CONDITIONS, AND PHASE IDENTIFICATION (X-RAY AND E.D. ANALYSES)

	Ideal composition			Starting composition			Thermal treatment				
n	Bi	Sr	Cu	Bi	Sr	Cu	Synthesis T (°C)	Annealing T (°C)	t (hr)	Atmosphere	X ray
4	8	16	10	8.3	15.8	10	880	880	96	air	Pure
5	10	18	11	10.6	17.0	11	750	840	84	air	Majority (>80%)
6	12	20	12	12.0	18	12	880	880	96	air	Majority (>80%)
7	14	22	13	13.0	19.5	13	800	800	96	air	Pure

tion patterns of the $n = 4$ to $n = 7$ members are given in Fig. 2. A characteristic variation of the intensity of the reflections is observed along B, with a sequence of $n + 1$ weak spots followed by two intense spots; this modulation allows a rapid identification of the n value to be ensured. Moreover the E.D. patterns are not always so perfect since some diffuse weak streaks or extra reflections are sometimes observed, especially for high n values, attesting to the presence of defective n' members different from the n nominal value. Two examples are shown in Figs. 3a and 3b. In the first one, diffuse streaks are observed along B with nodes corresponding to the tubular-7 member (Fig. 3a); in the second one (Fig. 3b), the superposition of two patterns, $n = 5$ and $n = 6$, is observed, showing that no regular intergrowth between the two members has been achieved. The [100] E.D. patterns are given in Fig. 4. The reconstruction of the reciprocal space was performed for each member; it appears that the reflection conditions lead to the *Bbab* space group for even n members (4 and 6) and the *Bmmm* space group for uneven n members (5 and 7). According to these observations, the cell parameters were determined. Variations of the parameters are observed with the cationic content; as an example, for the tubular-7 member one observes $a =$

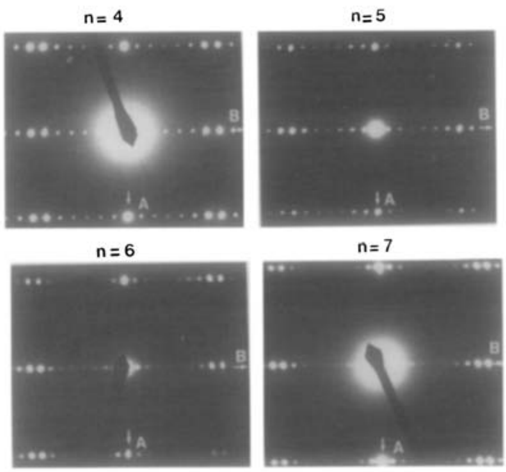

FIG. 2. Typical [001] electron diffraction patterns of the $n = 4$ to $n = 7$ members of the orthorhombic tubular family.

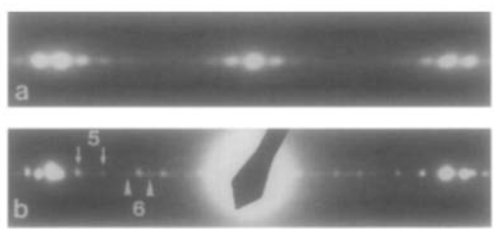

FIG. 3. (a) Diffuse streaks or (b) extra spots corresponding to the superposition of two patterns ($n = 5$ and $n = 6$ in this example) are often observed for members $5 \geq n \geq 7$.

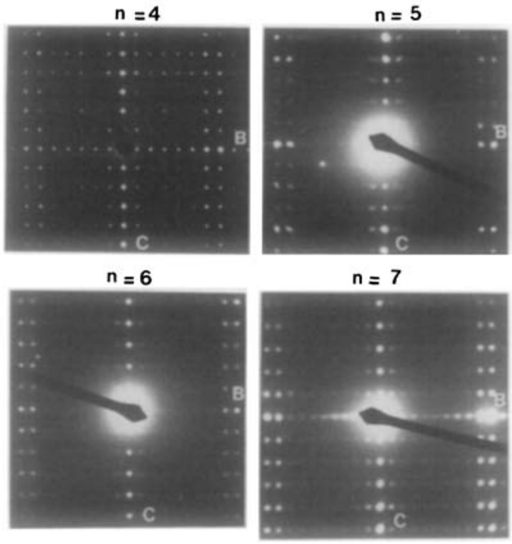

FIG. 4. [100] electron diffraction patterns.

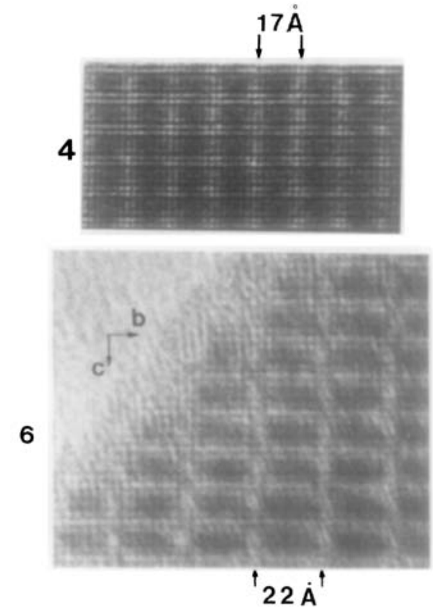

FIG. 5. Examples of [100] images of n = 4 (a) and n = 6 (b) members.

5.393 Å, b = 24.593 Å, and c = 24.373 Å for the starting composition, 14/22.3/13, whereas a = 5.390 Å, b = 24.683 Å, and c = 24.370 Å for 13.0/21.7/13; one observes that the b parameter is more sensitive to the composition. Mean cell parameters are given in Table II; it can be seen that the a axis remains constant, whereas the c parameter increases with the n value.

The HREM images recorded along [100] allowed our hypothesis on the structural mechanism to be confirmed, other orientations leading to images very similar to those recorded for the 2201 oxide. The images exhibit a "brick wall"-like contrast, made of rectangles whose width is characteristic of the n value; n = 4 and n = 6 members are shown as examples in Figs. 5a and 5b, and b = 7 in Fig. 9a. It should be noted that for $n > 4$, intergrowth defects and domains are observed, in agreement with the E.D. observations.

Along [001], no direct correlation with the

TABLE II

$(Bi_2Sr_2CuO_6)_n(Sr_8Cu_6O_{16}$ MEAN EXPERIMENTAL CELL PARAMETERS

n	a (Å)	b (Å)	c (Å)	Space group
4	5.37	33.9	23.97	*Bbab*
5	5.37	19.3	24.09	*Bmmm*
6	5.38	44.1	24.25	*Bbab*
7	5.39	24.6	24.37	*Bmmm*

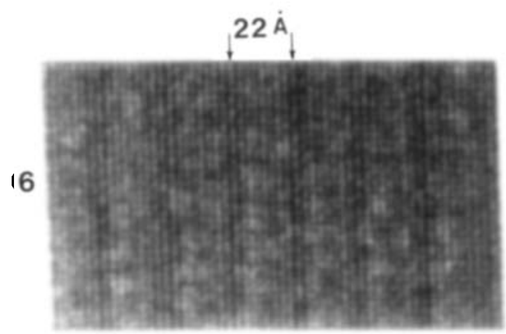

FIG. 6. [001] image of a n = 6 member.

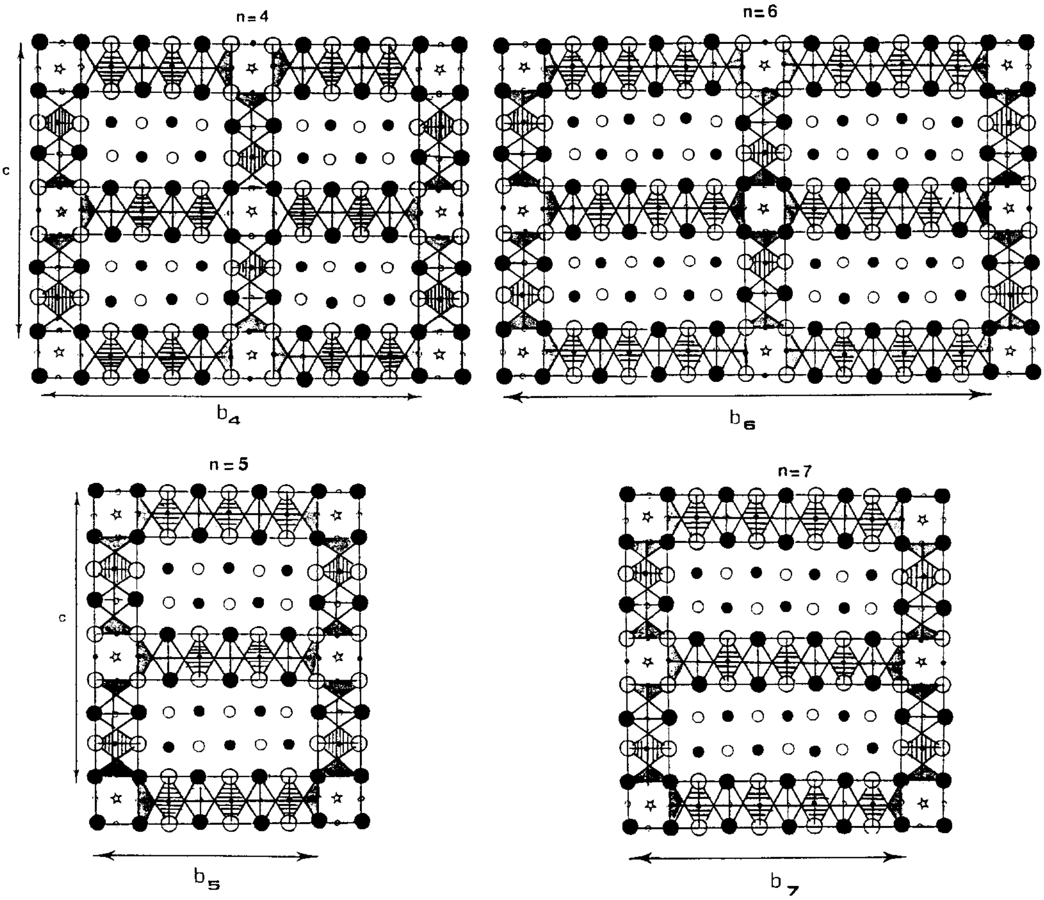

FIG. 7. Ideal drawing of the members n = 4, 5, 6, and 7 of the orthorhombic tubular family.

atomic arrangement can be made, owing to the mean projection of the ions of the different layers; the strontium–copper–oxygen layers of the perovskite-like units, slightly more spaced than those of the 2201 type, evidence the periodicity along the b axis; the n = 6 member is shown as an example in Fig. 6. It should be noted that these images are quite similar to those recorded along [001] in the 2201 and 2212 bismuth superconductors (*3, 9–10*).

The Orthorhombic Tubular Oxides

A new family of copper oxides has been isolated and characterized. It results from the intergrowth along the $\vec{b}$ axis, of n 2201-type slices with a perovskite-related slice; the general formulation $(Bi_{2+x}Sr_{2-x}CuO_{6+\delta})_n(Sr_{8-x'}Cu_6O_{16+y})$ expresses this structural mechanism.

The ideal cell of the different members constituting this new family can be easily calculated, taking in reference the cubic perovskite subcell. Owing to the relative positions of the cations, two types of n values, even or odd, must be distinguished. For even members, the thickness of the different units must be doubled for periodicity, contrary to the odd members (Fig. 7). The ideal parameters are given in Table III.

It should be noted that the n = 2 member,

TABLE III

CALCULATED LATTICE PARAMETERS OF THE IDEAL $(Bi_2Sr_2CuO_6)_n(Sr_8Cu_6O_{16})$ MEMBERS

n	Ideal parameters
Even	$a_n \approx 2a_p\sqrt{2} \approx a_{2201} \approx 5.4$ Å $b_n \approx \left[(n+1)a_p\frac{\sqrt{2}}{2} + a_p\right] \times 2$ $c \approx \left[a_p + \frac{3}{2}a_p\sqrt{2}\right] \times 2 \approx c_{2201} \approx 24$ Å Ideal space group type: F
Uneven	$a_p \approx 2a_p\sqrt{2} \approx a_{2201} \approx 5.4$ Å $b_n \approx (n+1)a_p\frac{\sqrt{2}}{2} + a_p$ $c \approx \left[a_p + \frac{3}{2}a_p\sqrt{2}\right] \times 2 \approx c_{2201} \approx 24$ Å Ideal space group type: B

whose idealized structure is shown in Fig. 8, would exhibit, if it exists, the layer stacking mode of the 2201 structure along $\vec{b}$ and $\vec{c}$ and, thus, a tetragonal cell.

The Other Members

Though they were not observed by X-ray diffraction, the different members corre-

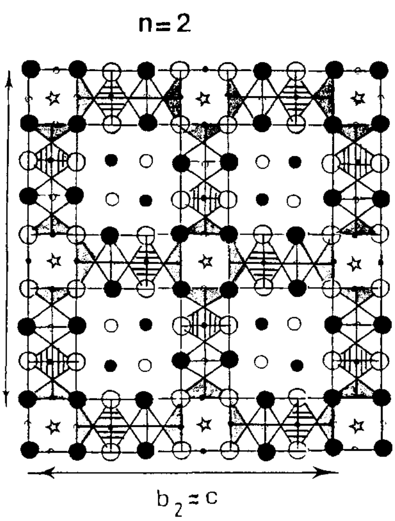

FIG. 8. Hypothetical tetragonal $n = 2$ member.

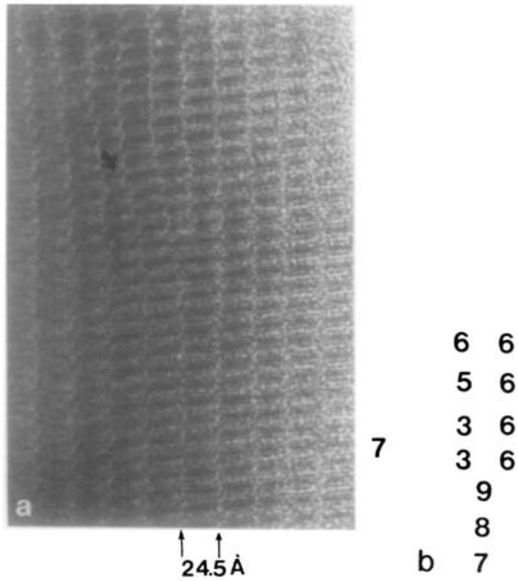

FIG. 9. (a) Example of a superdislocation-like defect. In such defects, low n members ($n < 4$) or high n members ($n > 7$) can be locally stabilized. (b) n values at the level of the "fork" of the superdislocation-like defect.

sponding to low and high n values, $n < 4$ and $n > 7$, can be observed in the form of extended defects.

Low n values. During our investigation of samples with a nominal composition corresponding to $n < 4$, no crystallite of the $n = 1$, 2, or 3 member has been observed. The X-ray and E.D. diffraction patterns gave evidence of mixtures of Sr_2CuO_3, $SrCuO_2$, 2201, or tubular-4 grains. Moreover, it should be noted that the low n value members ($n < 4$) are sometimes observed in disturbed crystals of a nominal composition corresponding to a nonintegral or high n value ($n > 6$). In such samples we indeed observed aleatory sequences of tubular members along the $\vec{b}$ axis; moreover, concerted variations of n from one slice to the adjacent along the $\vec{c}$ axis are sometimes visible, leading to a "superdislocation" mechanism. An example is shown in Fig. 9a. In such areas low n members are often locally stabilized; in this example, a row of $n = 3$ members is observed (curved arrow), whereas two other tubular-3 members are formed at the level of the fork of the superdislocation (Fig. 9b).

High n values. In samples with nominal compositions $n > 7$, we have never observed crystallites whose E.D. patterns give evidence of the stabilization of tubular-8 or higher members; moreover, they have never been imaged in the form of extended domains in defective crystals. In fact, they are observed at the level of superdislocation-type defects, where they can be stabilized in the form of a single unit. For instance, Fig. 9 shows that $n = 8$ and $n = 9$ units are observed at the connection of two adjacent $n = 3$ and $n = 6$ units with a single $n = 7$ unit; the intermediate members are $n = 9$ and $n = 8$.

The issue of the existence of the high n values ($n > 7$) can be raised; in the families built up from the intergrowth of two structural units such as the tungsten bronzes or the phosphate tungsten bronzes, the high members can be isolated only with difficulty as single phases but are observed in the form of crystallites or domains in the matrix of disturbed crystals. One of the explanation to such a feature could be correlated to the width of the 2201 slice. The tubular-7 oxide exhibits indeed a periodicity of 25 Å along the b axis, whereas the $n = 8$ member would correspond, according to the structural relationships, to 27.5 Å, i.e., a periodicity for which the modulated undulations of the Bi–O layers are observed. This suggests that the undulations which probably result from the stereoactivity of the $6s^2$ lone pair of Bi^{III} take place only when a minimum of adjacent bismuth atoms is observed.

Concluding Remarks

From this work, it appears that a new structural family has been characterized. Its structure is built up from the regular intergrowth of 2201-type slices with a perovskite-related unit, according to the formulation $(Bi_{2+x}Sr_{2-x}CuO_6)_n(Sr_{8-x'}Cu_6O_{16+y})$. Four regular members, $n = 4$, 5, 6, and 7, have been isolated. The high resolution electron microscopy of this family, essential to understanding the structural mechanism which governs the stabilization of these phases, is in progress.

Acknowledgments

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