

## Preferential Crystallographic Site Substitution and Oxygen Migration in $\text{Bi}_2\{\text{Sr}, \text{Ca}, \text{Ln}\}_3\text{Cu}_2\text{O}_8$ Related to Rare Earth Ion Size ( $\text{Ln} = \text{La}, \text{Yb}$ )

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Received June 18, 1990; in revised form September 28, 1990

Substitution of rare earths of various size (i.e., La and Yb) in the superconducting 2212 phase  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Ln}_y\text{Cu}_2\text{O}_{8+x+y/2}$  ( $0 \leq y \leq 1$ ) shows: (i) the larger La atoms substitute preferentially on the Sr site while the small Yb atoms occupy the Ca site; (ii) the superconductive property disappears when  $y$  reaches 0.5; (iii) as the Yb-doped phase approaches  $y = 0.5$  the oxygen layers sandwiched between the Bi layers rearrange; an effect which may be associated with the observed variation of the modulation vector of the superstructure and, subsequently, with the phenomenon of superconductivity. Various phases corresponding to  $y = 0.1, 0.2, 0.3, 0.4,$  and  $0.5$  have been identified as separate through powder and single crystal diffraction, X-ray techniques, and electron microscopy investigations and their superconductivity properties checked by four probe resistivity measurements. © 1991 Academic Press, Inc.

### Introduction

In previous papers, the preparation of rare earth "cocktails"  $\text{Ln}$  (formally, an analog of the "mischmetal") in which equal amounts of up to five different rare earths are simultaneously substituted for Y in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  superconductors has been described: phases corresponding to Ce and Pr homologues with average ionic radii  $r_{\text{Ln}} = r_{\text{Ce}}$  or  $r_{\text{Ln}} = r_{\text{Pr}}$  were shown to be superconducting phases ( $T_c$  above 85 K) (1-2). These phases exhibit remarkably facile  $\text{Ln}$  cation random distribution among their crystallographic sites and hence homogeneous crystalline samples. These properties are now used to prepare new members related to the structural family  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (3-7).

In this study, two rare earth with very different ionic radii size, a large one: lanthanum ( $r_{\text{La}} = 1.18 \text{ \AA}$ ) and a small one: Yb ( $r_{\text{Yb}} = 0.98 \text{ \AA}$ ) (8) were chemically substituted for Ca in the material with the formula  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Ln}_y\text{Cu}_2\text{O}_{8+x+y/2}$ . Following these substitutions by X-ray powder investigation it appeared that probably two mechanisms were taking place with regard to the size of the rare earth. A full study, involving crystal growth and X-ray single crystal determinations, was then developed in the case of the ytterbium for calcium substitutions.

The basic idealized structural model used in a first attempt, convenient for our propose, derives from Schnering's space group (4) (No. 66,  $Cccm$ ) with cell parameters re-

lated to Tarascon's (3). Taking into account the proposals developed by Andersson *et al.*, and Galy *et al.* (9–11) concerning the structural chemistry of "lone pair  $E$  elements," (the lone pair  $E$  associated with bismuth takes roughly the space of an oxygen), such a structure appears to be a rather compact network, unitary volume  $v = \text{cell volume}/\text{number of O, Sr, Ca}$ ,  $E_{\text{Bi}} = 17 \text{ \AA}^3$ , (example  $16 \text{ \AA}^3$  in  $\text{TiO}_2$ ), formular  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8E_2$ .

It was found in this work that Ca and Sr occupy two sites (4f and 8l) equivalent to that published by Schnering. However a study of site occupancy shows that Ca and Sr can be partially exchanged. Our results are in agreement with previous work (6) reporting this substitution, illustrated by the formula  $\text{Bi}_2[\text{Sr}_{2-z}\text{Ca}_z]^{(8l)}[\text{Ca}_{1-z}\text{Sr}_z]^{(4f)}\text{Cu}_2\text{O}_8E_2$ , with  $0 \leq z \leq 1$ .

## Powder Studies (La, Yb)

### 1 Experimental

The samples corresponding to the compositions  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Ln}_y\text{Cu}_2\text{O}_{8+x+y/2}$  with  $0 \leq y \leq 1$  and  $x$  being the extra amount of oxygen due to a possible oxidation of copper (II) were prepared using the starting materials  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Yb}$ ),  $\text{SrCO}_3$ , and  $\text{CaCO}_3$  in stoichiometric ratios. The carefully ground oxides were fired at increasing temperature in the range  $825\text{--}880^\circ\text{C}$  for  $0 \leq y \leq 0.6$  and  $870^\circ\text{C}$  in the remaining cases. The samples were quenched, pelletized, and sintered at  $875\text{--}900^\circ\text{C}$  for samples corresponding to  $y \leq 0.6$  and  $890^\circ\text{C}$  for the others; all these experiments were performed in air. The sintering time varied from 24 hr up to 90 hr depending on the amount of substituted rare earth. The cooling rate was around  $200^\circ\text{C}/\text{hr}$ . All the samples were characterized by their X-ray powder pattern ( $\text{CuK}\alpha$  radiation) and by four probe resistivity measurements.

## 2 Results

*Yb case.* From X-ray analysis of the various samples it was possible to determine the variation of cell parameters, using an orthorhombic cell:  $b$  and  $c$  are roughly the same, while  $a$  decreases significantly (see Fig. 1). In the diffractograms, for  $y$  values above 0.5, other peaks appear which were assigned to the presence of at least one extra phase, i.e.,  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ . Nevertheless, in this complicated multidimensional phase

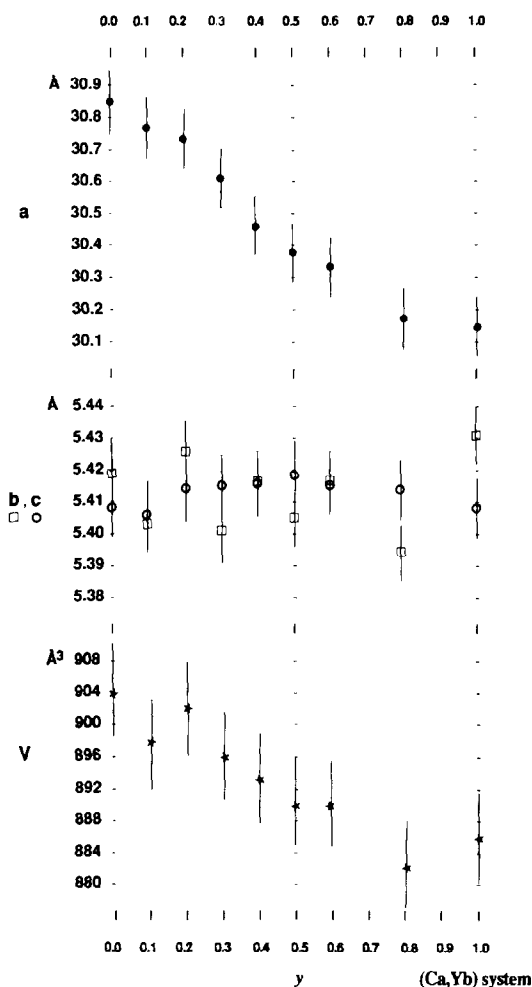


FIG. 1. Variation of lattice parameters with  $y$  in  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$ .

diagram, the cell parameters continue to vary, indicating that the phase  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  develops its domain in another way, i.e., another set of substitutional or nonstoichiometric parameters.

It appears from a comparison of theoretical calculations of the intensity of all the peaks with experimental powder patterns that Yb atoms preferentially substitute for Ca (site 4f); the most sensitive reflections being 200 and 511, which decrease in intensity, and the 400 reflection, which increases.

The temperature dependence of the resistivity of various phases (from which we extracted  $T_c$ ) exhibits very similar evolution to that shown by the Y-substituted compounds published by Yoshizaki *et al.* (12). They are superconductors for  $y < 0.5$  (see

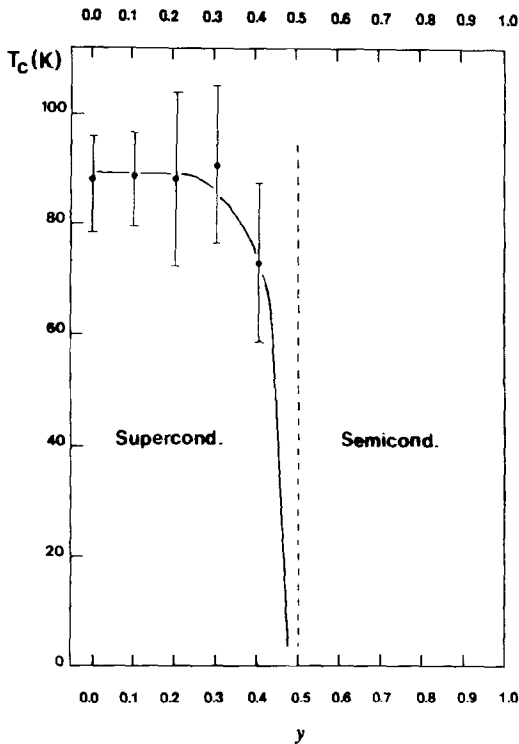


Fig. 2.  $T_c$  versus  $y$  in  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  (bars represent  $\Delta T$  between onset and  $R_0$ )

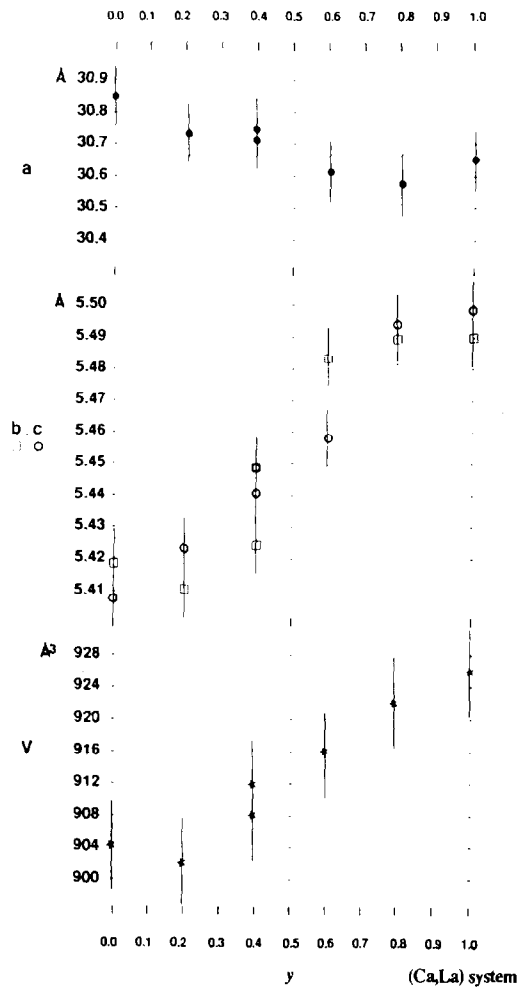


Fig. 3. Variation of lattice parameters with  $y$  in  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{La}_y\text{Cu}_2\text{O}_{8+x+y/2}$ .

Fig. 2). At higher  $y$  values, 0.5 to 1.0, resistivity measurements indicate a semiconductor behavior, the conductivity decreasing when  $y$  increases.

*La case.* In an analogous way it is demonstrated that the phase  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{La}_y\text{Cu}_2\text{O}_{8+x+y/2}$  extends up to  $y = 0.5$ . The variation of the lattice parameters (see Fig. 3) is rather different from the previous case (Yb):  $b$ ,  $c$  increase with a point of inflection of the curve around  $y = 0.5$ ;  $a$  decreases, but less than for Yb, and exhibits again a

change in the evolution around 0.5, indicating a possible ordering phenomenon or a variation in the substitution mechanisms. By comparing calculated and measured diffraction intensities it was possible to propose that La was substituting preferentially in the Sr site (8l): the sensitive 200 reflection decreases but less than in the Yb case; the 400 reflection does not emerge from the background; the 511 reflection is unaffected. To confirm these observations, some experiments in which La was substituted for Sr ( $\text{Bi}_2\text{Sr}_{2-y}\text{La}_y\text{CaCu}_2\text{O}_{8+x+y/2}$ ) were performed; they gave very similar powder patterns with respect to position and intensity of the peaks. First studies for a small  $y$  value, i.e.  $y = 0.2$ , shows a superconductive behavior of the phase.

### X-Ray Single Crystal Studies (Yb)

#### 1 Experimental

To investigate the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  solid solutions and to elucidate the possible structural modifications near the super-semiconductor transition, crystals were grown using a flux method. The choice of the flux was based on the relationships between the stereochemical behavior of the lone pair elements; from a consideration of some close similarities between steric influences of the lone pairs Sn(II) and Bi(III) in oxide compounds (10, 11), it was decided to use SnO as a flux (13). Black single crystals of good quality and corresponding to the wanted formula  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  with  $y = 0.1, 0.2, 0.3, 0.4$ , or 0.5 (values of the starting preparation) were selected for X-ray investigations ( $\text{MoK}\alpha$ ). These compounds crystallize in the orthorhombic system with strong subcell parameters (Table I). They are in reasonably good agreement with the parameters derived from powder diffraction data although there is a small systematic variation, particularly in the  $a$  parameter (ap-

TABLE I  
SUBCELL PARAMETERS OF  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  SINGLE CRYSTALS ( $y$  VALUE OF THE STARTING PREPARATION)

$y$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
0.1	30.680(9)	5.410(1)	5.411(2)	898.0(4)
0.2 <sup>a</sup>	30.602(9)	5.4109(6)	5.4046(6)	894.9(3)
0.3	30.51(1)	5.415(1)	5.409(1)	893.6(4)
0.4 <sup>a</sup>	30.38(2)	5.410(2)	5.408(2)	888.8(6)
0.5	30.33(2)	5.417(2)	5.410(3)	888.9(6)

<sup>a</sup> Selected crystals for structural determination.

proximately 0.2%): such discrepancy is reasonably accounted for by uncertainty on the stoichiometry of the single crystal (rough estimation  $\Delta y \leq 0.05$ ), and also with the ones published by Von Schnering *et al.* (4) and Tarascon *et al.* (3). These phases exhibit modulated structures whose modulation wave vector  $q$  is directly correlated with the degree of Yb substitution as demonstrated in the laboratory by Casanove *et al.* (14) on the same batch of single crystals: the ratio  $|b^*/q|$  decreases from 4.75 to 4.33 when  $y$  evolves from 0 to 0.5.

#### 2 Structural Results

The present results concern the crystal structures for  $y = 0.2$  and 0.4. These compositions, selected for single crystal studies, represent compounds situated in two positions of the  $T_c$ 's graph,  $y = 0.2$  being the superconductor with the highest  $T_c$  value and  $y = 0.4$  a phase close to the transition super-semiconductive behavior exhibiting a noticeable decrease in the  $T_c$  (Fig. 2). The crystal structure solutions are for an average structure which cannot fulfill completely the atomic details of the superconductor, since the reflections indicating the modulation have not yet been taken into account. Nevertheless all the subcell  $hkl$  reflections observed corresponding to the  $Cccm$  space group have been used in the calculations. Tables II and III summarize

TABLE II  
EXPERIMENTAL CONDITIONS FOR THE STRUCTURAL ANALYSIS OF  
 $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.60}\text{Yb}_{0.40}\text{Cu}_2\text{O}_{8+x+y/2}$

	$y = 0.2$	$y = 0.4$
Subcell crystal system	Orthorhombic	
Space group	$Cccm$ No. 66	
Crystal size (mm)	$0.20 \times 0.10 \times 0.016$	$0.25 \times 0.15 \times 0.015$
Calculated density ( $\text{g} \cdot \text{cm}^{-3}$ )	6.79	7.04
Radiation	$\text{MoK}\alpha$	
Wavelength ( $\text{\AA}$ )	0.71073	
Scan mode	$\omega - 2\theta$	
$2\theta$ range ( $^\circ$ )	2–62	2–60
No. of recorded reflections	1858	1583
No. of unique observed reflections ( $I > 2\sigma$ )	326	408
Absorption correction mode	Empiric (16)	Numeric (17)
Linear absorption coefficient ( $\text{cm}^{-1}$ )	569	596
Transmission factor range	0.14 to 1.0	0.20 to 1.0
No. of refined parameters	34	44
Secondary extinction	$5.2 \times 10^{-8}$	$1.6 \times 10^{-7}$
Final $R$	0.117	0.099
Final $R_w$	0.108	0.105

the experimental conditions and refined atomic parameters. The heavy atoms are treated anisotropically while the oxygens are kept isotropic. The CY atom represents the mixture  $(1 - y)\text{Ca} + y\text{Yb}$ . In the  $y = 0.4$  phase the Bi atoms are more disordered and their contribution is represented by two extreme positions, Bi(1) and Bi(2) (two sites distant by  $0.23 \text{ \AA}$ ); in the meantime the O(4) and O(5) oxygen sites are partially occupied. The presence of oxygen in O(5) implies the insertion of extra oxygens between Bi layers. The occupancy of the O(5) site due to  $\text{Yb}^{3+}$  for  $\text{Ca}^{2+}$  substitution is also associated with the diminution of the one of O(4), indicating that the migration of some oxygen O(4) to the O(5) plane has occurred. The sites of occupancy of O(4) and O(5) were carefully varied and locked in order to refine reasonably the  $B$  factors.

Figures 4 and 5 illustrate the oxygen environment of the heavy atoms and their stacking sequence for  $y = 0.2$  and  $y = 0.4$ :

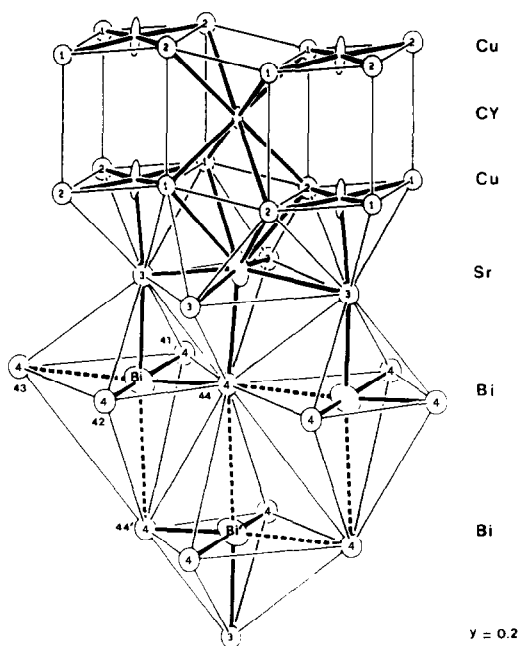


FIG. 4. Perspective view of the average structure of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  for  $y = 0.2$ .

TABLE III  
 ATOMIC PARAMETERS FOR  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.60}\text{Yb}_{0.40}\text{Cu}_2\text{O}_{8+y/2}$

$y = 0.2$						
Atom	Wyckoff notation	$x$	$y$	$z$	$B(\text{\AA}^2)$ eq. or iso*	Site Occupancy
Bi	8l	0.4479(1)	0.229(1)	0	4.65(8)	1
CY	4f	$\frac{1}{4}$	$\frac{3}{4}$	0	1.4(2)	1
Sr	8l	0.3596(3)	0.740(3)	0	3.3(2)	1
Cu	8l	0.3025(4)	0.252(3)	0	2.5(2)	1
O(1)	8g	0.299(1)	0	$\frac{1}{4}$	2.0(5)*	1
O(2)	8g	0.302(2)	$\frac{1}{2}$	$\frac{1}{4}$	3.5(7)*	1
O(3)	8l	0.371(1)	0.21(2)	0	4.1(1)*	1
O(4)	8l	0.445(1)	0.202(7)	$\frac{1}{2}$	2.7(6)*	1
Atom		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	
Bi		0.00093(3)	0.043(2)	0.046(2)	-0.0044(8)	
CY		0.0009(1)	0.005(2)	0.001(2)	0.000(1)	
Sr		0.0013(1)	0.022(2)	0.021(2)	-0.006(1)	
Cu		0.0014(1)	0.011(2)	0.010(2)	0.000(1)	
$y = 0.4$						
Atom	Wyckoff notation	$x$	$y$	$z$	$B(\text{\AA}^2)$ eq. or iso*	Site Occupancy
Bi(1)	8l	0.4484(2)	0.2191(8)	0	4.6(1)	0.5
Bi(2)	8l	0.4484(2)	0.261(2)	0	5.0(1)	0.5
CY	4f	$\frac{1}{4}$	$\frac{3}{4}$	0	2.1(1)	1.
Sr	8l	0.3602(3)	0.748(2)	0	4.1(1)	1.
Cu	8l	0.3019(3)	0.250(1)	0	2.8(2)	1.
O(1)	8g	0.303(1)	0	$\frac{1}{4}$	1.6(6)*	1.
O(2)	8g	0.292(2)	$\frac{1}{2}$	$\frac{1}{4}$	2.6(8)*	1.
O(3)	8l	0.382(2)	0.28(1)	0	6.2(2)*	1.
O(4)	8l	0.429(2)	0.14(1)	$\frac{1}{2}$	3.1(1)*	0.60
O(5)	16m	0.495(6)	0.15(2)	0.24(7)	4.2(2)*	0.25
Atom		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	
Bi(1)		0.00078(4)	0.012(1)	0.081(4)	-0.0020(6)	
Bi(2)		0.00061(4)	0.094(4)	0.014(1)	0.006(1)	
CY		0.00160(9)	0.001(1)	0.003(1)	0.0003(7)	
Sr		0.0018(1)	0.030(2)	0.017(2)	-0.002(1)	
Cu		0.0019(1)	0.005(1)	0.006(1)	0.0002(9)	

Note.  $B_{\text{eq.}} = 4/3 \sum_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j) \beta_{ij}$ .  $\beta_{13}$  and  $\beta_{23}$  are fixed to 0 due to space group symmetry; the form of anisotropic displacement parameter is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

Cu atoms are fourfold coordinated to O(1) and O(2). In  $y = 0.2$  they make a square with  $\text{O}(1)\text{--O}(1) = \text{O}(2)\text{--O}(2) = 2.702(3) \text{\AA}$  and  $\text{O}(1)\text{--O}(2) = 2.707(2) \text{\AA}$ . In  $y = 0.4$ , the corresponding values are 2.704(2) and 2.726(7)  $\text{\AA}$ . The bonds Cu–O(1) and Cu–O(2) (Table IV) compare well with previous reported values. O(3), at the apex of a square pyramid, may also be a participant in the copper coordination poly-

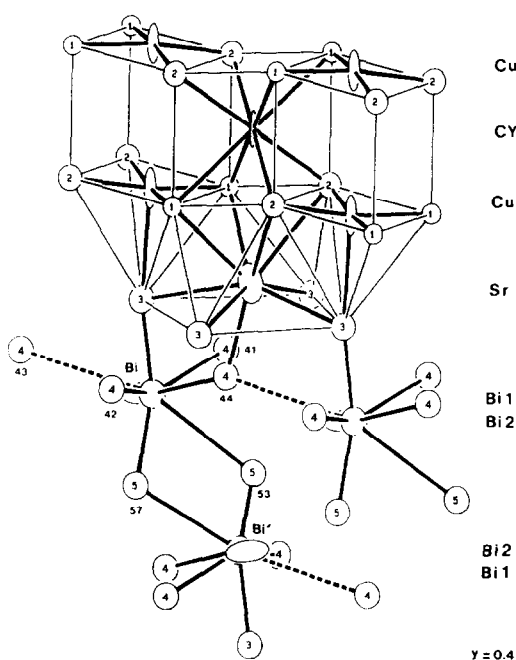


FIG. 5. Perspective view of the average structure of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Yb}_y\text{Cu}_2\text{O}_{8+x+y/2}$  for  $y = 0.4$ .

hedron. A variation of the Cu–O(3) distance (2.10 Å for  $y = 0.2$  to 2.44 Å for  $y = 0.4$ ) is observed but the deviation of the copper atom from the oxygen plane (0.08 and 0.04 Å, respectively, for  $y = 0.2$  and  $y = 0.4$ ) does not seem significant when compared with the strong thermal anisotropy along the  $a$  axis (root mean square amplitudes: 0.26 and 0.30 Å).

CY atoms are in an oxygen tetragonal prism; CY–O calculated average distances (Table IV) are in good agreement with the data of Shannon and Prewitt (8). The CuO layers are puckered ( $165^\circ$  for  $y = 0.2$  and  $166^\circ$  for  $y = 0.4$ ).

Sr atoms are in a monocapped Archimedean square antiprism built of O(1), O(2), and O(3). The Sr–O distances (Table IV) are homogeneous in the  $y = 0.2$  case. For  $y = 0.4$ , Sr–O(4) is shortened. Due to a decreased occupancy on the O(4) site in  $y =$

0.4 the Sr atoms have a CN varying from 9 to 8.

Bi atoms in  $y = 0.2$  have two oxygen atoms at short distances (O(3) at 2.36 and O(4) at 2.34 Å) and three O(4) atoms at 2.708, 3.08, and 3.28 Å. The coordination polyhedra can be described as a large distorted octahedron with two more distant oxygen atoms being repelled to a secondary coordination sphere by the lone pair on Bi. The coordination of the Bi atom appears to be of the one-sided 4 + 1 type; a trigonal bipyramid with two oxygens, O(3) and O(44), and the lone pair  $E$  in the equatorial plane and two oxygens O(41) and O(42) at the apices. The rather large spaces between the bismuth layers are occupied by the lone pairs  $E$ ; this structure is in agreement with the Tarascon's model (3). The amount of extra oxygen seems to be too small to be detected directly or by indirect influence on the structural organization.

TABLE IV  
SELECTED ATOMIC DISTANCES (Å)

$y = 0.2$			
Bi–O(3)	2.36(5) × 1		
Bi–O(44) <sup>a</sup>	2.34(4) × 1		
Bi–O(41,42)	2.708(3) × 2		
Bi–O(43)	3.08(4) × 1		
Bi–O(44')	3.28(4) × 1		
Sr–O(1)	2.69(3) × 2	CY–O(1)	2.43(2) × 4
Sr–O(2)	2.55(3) × 2	CY–O(2)	2.51(3) × 4
Sr–O(3)	2.60(7) × 1		
Sr–O(3)	2.734(9) × 2	Cu–O(1)	1.92(1) × 2
Sr–O(3)	2.86(7) × 1	Cu–O(2)	1.90(1) × 2
Sr–O(44)	2.63(5) × 1	Cu–O(3)	2.10(5) × 1
$y = 0.4$			
Bi(1)–O(3)	2.05(6) × 1	Bi(2)–O(3)	2.02(7) × 1
Bi(1)–O(44)	2.02(7) × 1	Bi(2)–O(44)	2.24(8) × 1
Bi(1)–O(41,42)	2.80(2) × 2	Bi(2)–O(41,42)	2.84(2) × 2
Bi(1)–O(43)	3.52(7) × 1	Bi(2)–O(43)	3.30(8) × 1
Bi(1)–O(51,57) <sup>a</sup>	2.0(3) × 2	Bi(2)–O(51,57)	2.0(3) × 2
Bi(1)–O(52,58)	2.3(3) × 2	Bi(2)–O(52,58)	2.30(3) × 2
Bi(1)–O(53,55)	2.8(2) × 2	Bi(2)–O(53,55)	3.0(2) × 2
Bi(1)–O(54,56)	2.9(2) × 2	Bi(2)–O(54,56)	3.1(2) × 2
Sr–O(1)	2.59(3) × 2	CY–O(1)	2.50(2) × 4
Sr–O(2)	2.82(3) × 2	CY–O(2)	2.30(2) × 2
Sr–O(3)	2.61(8) × 1		
Sr–O(3)	2.79(2) × 2	Cu–O(1)	1.913(5) × 2
Sr–O(3)	2.96(8) × 1	Cu–O(2)	1.937(8) × 2
Sr–O(44)	2.2(1) × 1	Cu–O(3)	2.44(7) × 1

<sup>a</sup> 41 to 44 and 51 to 58 correspond to sites O(4) and O(5) (Figs. 4 and 5).

The surrounding of Bi atoms in the  $y = 0.4$  structure shows drastic differences: the extra oxygens are present in sufficient amounts to perturb and reorganize the structure between the Bi planes. A new oxygen site is located in O(5) and its occupancy is in accord with the stoichiometry of the compound and with a correlated diminution of the O(4) site occupancy. A double oxygen bridge appears between Bi atoms in adjacent planes, for example:  $\text{Bi}-\text{O}(57) = 2.0 \text{ \AA}$ ,  $\text{O}(57)-\text{Bi}' = 2.9 \text{ \AA}$  and  $\text{Bi}-\text{O}(53) = 2.8 \text{ \AA}$ ,  $\text{O}(53)-\text{Bi}' = 2.3 \text{ \AA}$ .

Obviously significant changes must occur between Bi layers, where lone pairs  $E$  and oxygens O(5) have to be accommodated. The coordination polyhedron  $\text{Bi}-E-\text{O}$  is twisted and the new distribution of  $\text{Bi}-\text{O}$  bonds implies a more three-dimensional character to the structure, the layers  $[\text{Bi}_2\text{Sr}_2\text{Ca}_{0.6}\text{Yb}_{0.4}\text{Cu}_2\text{O}_8]_n$  now being linked.

The results are the following:

(i) In the phases without rare earths or still with small amounts ( $y = 0.2$ ), the O(4) oxygen layer found by many authors (3, 4, 7) exists roughly at the level ( $x$  coordinate) of the bismuth; the separation between these layers is  $\Delta\text{O}(4) \cong 3.1 \text{ \AA}$ , close to  $\Delta\text{Bi} \cong 3.2 \text{ \AA}$ .

(ii) For the substituted compounds, when  $y$  is 0.4, these O(4) layers move further apart,  $\Delta\text{O}(4) \cong 4.2 \text{ \AA}$  compared with the same  $\Delta\text{Bi} \cong 3.2 \text{ \AA}$ , and they lose some oxygens; a supplementary layer of oxygen O(5) is intercalated midway between Bi layers, accepting the oxygens corresponding to  $y/2$  plus extra oxygens provided by the O(4) layers.

(iii) Imai *et al.* (6) who have reported an average structure for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  showing that  $\Delta\text{O}(4) \cong 1.2 \text{ \AA}$  have perhaps obtained a well-oxidized sample, the extra oxygens implying a move of the O(4) layer towards the space between Bi layers. Figure 6 schematizes this evolution. It is then reasonable to extrapolate that the oxygen organization evolves continuously at the

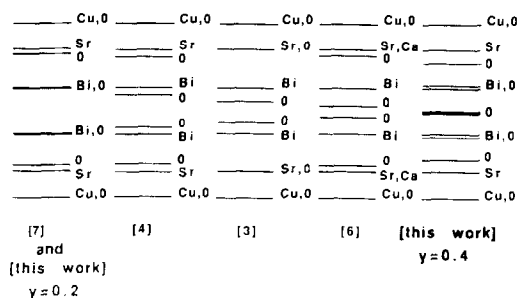


FIG. 6. Schematic representation of stacking sequences of various phases 2212.

level of O(4) and O(5) when the  $y$  parameter of substitution increases. This implies a direct interaction of these parameters with the variation of the modulation vector of these structures as followed by Casanove *et al.* (14) using electron microscopy techniques and perhaps with the vanishing of the superconductivity behavior of these phases.

(iv) These results are in agreement with work reported by Torardi *et al.* (15) concerning the nonsuperconducting  $\text{Bi}_2\text{Sr}_{3-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$  ( $x \cong 0.6$ ) phase, in particular the interatomic  $\text{Cu}-\text{O}$  distances (average  $1.94 \text{ \AA}$  in the base of square pyramid and  $2.44 \text{ \AA}$  for the oxygen of the apex) and also the description of the atomic arrangement with possible positions for extra oxygens in the  $\text{Bi}-\text{O}$  sheets. This last assumption by Torardi *et al.* offers for our work a clear indication of the location of these extra oxygens between Bi layers.

## Conclusion

The substitution of rare earth  $\text{Ln}$  (La, Yb) for calcium in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  phases does not affect the nature of their conductivity: they remain superconductive, up to  $y < 0.50$ , in spite of a probable different substitution mechanism. Indeed:

For a small ionic radius of  $\text{Ln}$ , i.e., Yb,



the substitution occurs on the calcium sites in tetragonal (pseudocubic) prisms very similar to the ones occupied by Y in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , the structural formula being  $\text{Bi}_2\text{Sr}_2[\text{Ca}_{1-y}\text{Yb}_y]^{(4f)}\text{Cu}_2\text{O}_{8+x+y/2}$ .

For the larger radii of La, the preferential site becomes the one of the strontium sites (8l) in a monocapped square antiprism, the remaining Sr atoms shifting consequently into the Ca sites (4f); the formula can be written  $\text{Bi}_2[\text{Sr}_{2-y}\text{La}_y]^{(8l)}[\text{Ca}_{1-y}\text{Sr}_y]^{(4f)}\text{Cu}_2\text{O}_{8+x+y/2}$ .

These investigations of the crystal structures show that a layer of oxygen is sandwiched almost midway between two Bi layers when  $y = 0.4$  and that the one situated at the bismuth level loses some of its oxygen atoms. Lone  $E$  pairs pointing toward the bismuth interspace for low  $y$  values are progressively tilted toward the Bi planes by the repulsive action of oxygen occupying the O(5) positions. Their stereochemical influence is responsible for linking the variation of the charge of the layers  $[\text{Sr}_2\text{Ca}_{0.6}\text{Yb}_{0.4}\text{Cu}_2\text{O}_8]_n$  to small displacements of Bi. These are related too with the evolution of the modulation vector and also to the transformation of the layer structure of this superconductor into a three-dimensional one, and contribute to the transition into the semiconductor state.

### Acknowledgments

Thanks are due to Dr. D. Lloyd and Pr. B. G. Hyde for comments on the manuscript, to M. J. Casanove and C. Roucau for electron microscopy investigation of various samples and most stimulating discussions. The authors are grateful to N. Cocuau and P. Cassoux for their assistance with four probe resistivity measurements.

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