

The Aptitude of Barium and Bismuth to Form Layered Cuprates : $\text{Bi}_2\text{Ba}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$, a 2201-Type Structure

A. Q. PHAM, M. HERVIEU, C. MICHEL,* AND B. RAVEAU

Laboratoire CRISMAT-Associé au CNRS, ISMRa Bd du Maréchal Juin, 14 050 Caen Cedex, France

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A bismuth barium cuprate, $\text{Bi}_2\text{Ba}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ with a layered structure has been synthesized for the first time for $0.50 \leq x \leq 1$. This oxide is isotypic with "2201" $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ superconductor, i.e., corresponds to the intergrowth of single BaCuO_3 perovskite layers with triple $[(\text{BiO})_2\text{BaO}]_x$ layers. The modulated character of the structure is documented and the possibility of inducing superconductivity in this structural type is discussed. © 1992 Academic Press, Inc.

Introduction

Bismuth strontium cuprates $\text{Bi}_2\text{Sr}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_{2m+4+\delta}$ and thallium barium cuprates $\text{Tl}_2\text{Ba}_2\text{Ca}_{m-1}\text{Cu}_m\text{O}_{2m+4+\delta}$ exhibit a great similarity. Both series of oxides are high T_c superconductors and are characterized by a layered structure corresponding to the intergrowth of oxygen-deficient perovskite layers (m copper sheets) with triple distorted rock salt layers $[(\text{SrO})(\text{BiO})_2]_x$ or $[(\text{BaO})(\text{TlO})_2]_x$. Curiously, all the attempts to synthesize barium bismuth cuprates isotypic with barium thallium cuprates were unsuccessful. Such a difference might be due to the size of Bi(III), much larger than that of Tl(III), and also to its particular electronic structure involving a $6s^2$ lone pair. Another explanation deals with the fact that in bismuth cuprates the syntheses are generally performed in air so that, in the presence

of barium, Bi(III) is more easily oxidized into Bi(V) than in the presence of strontium, so that phases of the Bi(V)-Ba-O system, and especially perovskites, could be stabilized. The recent synthesis of the 2212-superconductor in an argon flow, in the form of a stoichiometric pure oxide $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, without any excess oxygen (I), whereas the air prepared composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ always contains impurities, is in agreement with this viewpoint. In this work, we report the synthesis and characterization of a 2201-type phase $\text{Bi}_2\text{Ba}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$.

Experimental

The samples have been prepared by solid state reaction in nitrogen flow between the oxides Bi_2O_3 , La_2O_3 , CuO , and barium carbonate in adequate ratio according to the formulation $\text{Bi}_2\text{Ba}_{2-x}\text{La}_x\text{CuO}_y$. Mixtures of reactants were pelletized, heated at 810°C

* To whom correspondence should be addressed.

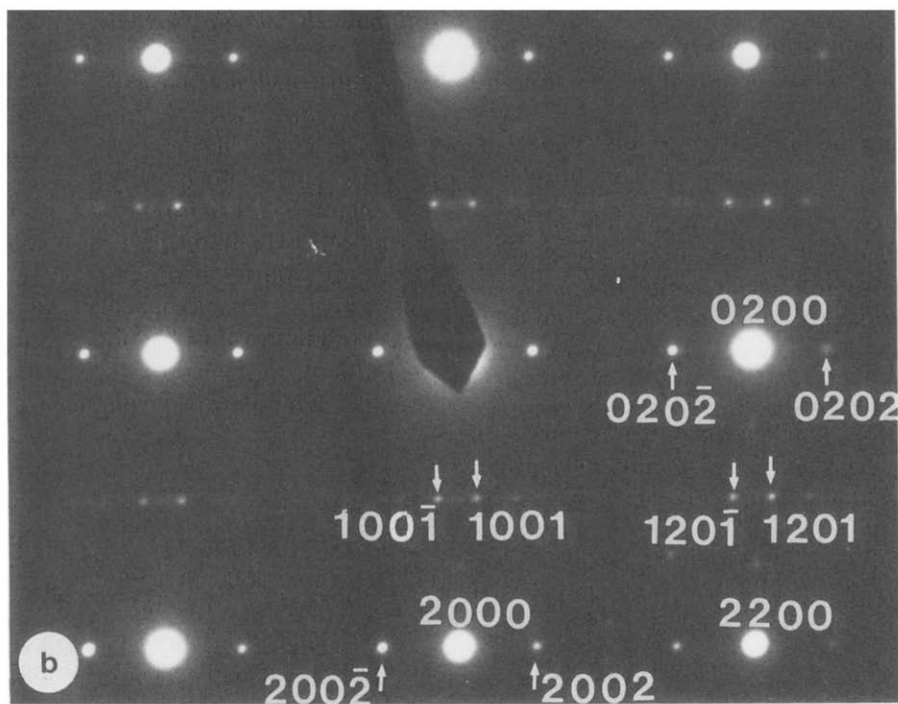
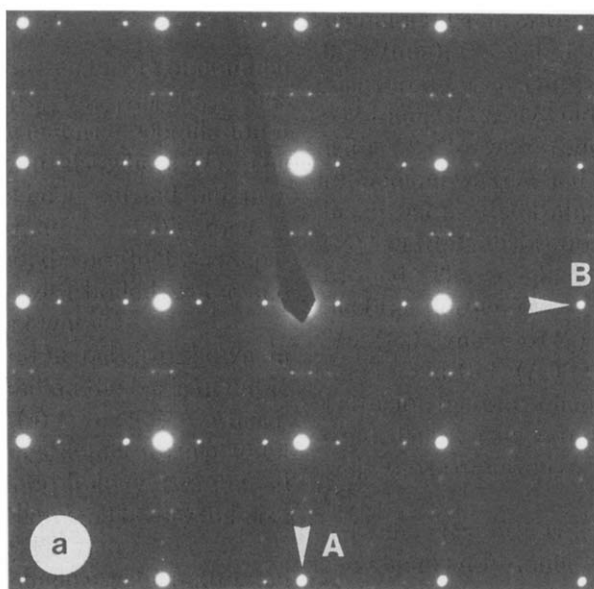


FIG. 1. (a) [001] electron diffraction pattern registered for $x = 1$; (b) indexation of the subcell reflections and satellites on an enlarged pattern.

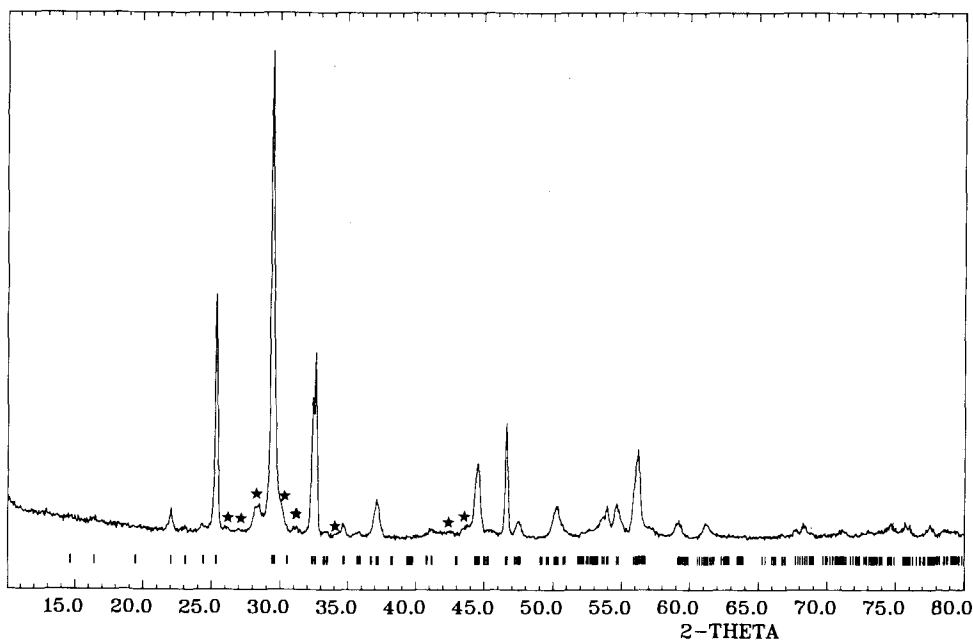


FIG. 2. Powder X-ray diffraction pattern of $\text{Bi}_2\text{BaLaCuO}_3$ ($10^\circ \leq 2\theta \leq 80^\circ$). The marks at the bottom of the figure correspond to the Bragg angles for the orthorhombic subcell. Satellite peaks are labeled by stars.

(± 10) for 48 hr. The powder X-ray diffraction data were collected in the range $10^\circ \leq 2\theta \leq 80^\circ$ by means of a vertical Philips diffractometer using the $\text{CuK}\alpha$ radiation. Bragg angle intensities were determined by profile fitting program and lattice constants were calculated by a classical least-squares refinement program.

Samples for electron diffraction study were prepared by a smooth crushing in alcohol; the crystals were deposited on a holey carbon film. Electron diffraction investigation was carried out using a Jeol 200CX electron microscope fitted with a side entry goniometer ($\pm 60^\circ$).

Results and Discussion

A single phase domain characteristic of the 2201-type structure is obtained for $0.50 \leq x \leq 1$. For $x > 1$, the X-ray diffraction

patterns show that, in addition to the peaks characteristic of the 2201-phase, some weak extra peaks appear which correspond to the oxygen deficient fluorite $\text{Bi}_8\text{La}_{10}\text{O}_{27}$ (2).

Electron diffraction investigation confirms the X-ray diffraction results and attests to the homogeneity of the sample. Systematic observations of more than hundred crystals, belonging to the single phase domain, did not cause any impurity to be detected. One observes a mica-like morphology of the crystals. The E.D. study gives evidence of satellites lying in incommensurate positions as shown from the [001]. The E.D. pattern (Fig. 1a) whose indexation concerning the main reflexions and satellites using h , k , l , and m as indices is given in Fig. 1b. The mean value of the incommensurate periodicity is of 3.83 along the B axis and the reflection conditions are $hk0m$ with $h + k + m = 2n$. Moreover, it is worth pointing

TABLE I
POWDER X-RAY DIFFRACTION DATA OF $\text{Bi}_2\text{BaLaCuO}_x$ IN THE RANGE $10^\circ \leq 2\theta \leq 51^\circ$
(FOR $\text{CuK}\alpha_1$ RADIATION)

<i>h</i>	<i>k</i>	<i>l</i>	<i>m</i>	d_{calc} (Å)	$2\theta_{\text{calc}}$	$2\theta_{\text{obs}}$	I/I_0
1	0	1	0	5.39	16.44	16.40	0.5
0	0	6	0	4.027	22.05	22.06	3.5
1	1	1	0	3.846	23.10	23.08	0.5
1	0	5	0	3.638	24.45	24.34	1.0
1	1	3	0	3.507	25.38	25.37	31.8
0	0	7	1	3.406	26.14	26.19	0.3
1	1	2	1	3.291	27.07	27.00	0.3
0	2	4	-2	3.165	28.17	28.17	3.5
0	2	1	-1	3.130	28.49	28.45	3.7
1	1	5	0	3.033	29.43	29.46	100.0
0	0	8	0	3.020	29.55		
1	1	6	-1	2.9811	29.95	30.05	3.3
1	1	4	1	2.9772	29.99		
1	2	3	-2	2.9797	31.03	30.98	1.1
2	0	0	0	2.7635	32.37	32.36	15.9
0	2	0	0	2.7460	32.58	32.59	20.8
1	2	0	-1	2.7421	32.63		
2	0	2	0	2.6939	33.23	33.33	2.4
0	2	2	0	2.6777	33.44		
1	0	8	1	2.6279	34.09	34.17	0.8
2	0	2	2	2.6101	34.33		
2	1	0	-1	2.5903	34.60	34.65	3.0
1	1	7	0	2.5836	34.69		
2	0	4	0	2.5130	35.70	35.78	1.2
0	2	4	0	2.4998	35.89		
1	2	1	0	2.4466	36.70	36.64	0.7
2	1	2	0	2.4186	37.14	37.13	10.9
0	0	10	0	2.4164	37.18		
1	0	9	0	2.4150	37.20	41.15	2.0
1	2	5	0	2.1919	41.15	41.14	
2	1	2	2	2.1588	41.81	41.78	0.9
1	1	10	-1	2.1220	42.57	42.53	0.9
2	1	7	-1	2.0720	43.65	43.66	1.0
2	2	1	-1	2.0720	43.65		
2	0	8	0	2.0391	44.39	44.36	7.6
0	2	8	0	2.0317	44.56	44.56	11.4
1	2	7	0	2.0029	45.24	45.31	1.1
2	0	8	2	2.0015	45.27		
2	2	0	0	1.9482	46.58	46.58	16.4
1	2	6	1	1.9466	46.62		
2	0	9	1	1.9130	47.37	47.47	1.6
1	1	11	0	1.9134	47.48		
2	1	8	0	1.9115	47.53	50.11	3.5
2	0	10	0	1.8184	50.11	50.04	
0	2	10	0	1.8142	50.25	50.27	4.9
3	0	3	0	1.7958	50.80	50.82	2.0

Notes. $a = 5.527$ Å, $b = 5.492$ Å, $c = 24.164$ Å, $q = 3.83$.

TABLE II
OXIDES $\text{Bi}_2\text{Ba}_{2-x}\text{La}_x\text{CuO}_x$: LATTICE CONSTANTS
(SUBCELL)

x	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	Impurity
0.5	5.521(2)	5.498(2)	24.250(6)	No
0.6	5.525(2)	5.492(2)	24.224(10)	No
0.8	5.532(2)	5.494(2)	24.197(8)	No
1.0	5.526(1)	5.492(1)	24.164(5)	No
1.1	5.535(2)	5.490(2)	24.110(10)	$\text{Bi}_8\text{La}_{10}\text{O}_{27}$
1.2	5.534(1)	5.489(1)	24.041(4)	"

out that the q vector, measured in more than 30 crystals, ranges from 3.7 to 3.9. This suggests an inhomogeneous distribution of the ions in the matrix, and especially of bismuth, barium, oxygen, and vacancies in the rock-salt-type layers.

In agreement with the E.D. results, the great majority of the X-ray diffraction peaks of the single phase domain could be indexed in the classical orthorhombic cell characteristic of the 2201-phase, as shown from the pattern of $\text{Bi}_2\text{BaLaCuO}_{6+\delta}$ (Fig. 2). The extra peaks (labeled by stars in Fig. 2) are very weak, since they exhibit an intensity smaller than 3% of the most intense peak of the pattern. Without any problem they can be considered as satellite reflections due to the incommensurate modulation. Indeed, preliminary study taking into consideration the only modulation along \mathbf{b} , shows that all these extra reflexions can be indexed with four indices h, k, l, m according to the equation

$$1/d^2 = \left(\frac{h}{a}\right)^2 + \left(\frac{k + (m/q)^2}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

in agreement with the reflection conditions used by Onoda *et al.* (3) for the "2212" bismuth cuprate. Of course, these observations do not rule out the existence of a possible modulation of the structure along other directions, i.e., along \mathbf{c} . Table I shows as an example the good accord between the

calculated and observed interplanar distances of the powder X-ray pattern of $\text{Bi}_2\text{BaLaCuO}_{6+\delta}$.

Indexing the X-ray patterns of different compositions of the whole domain in the classical orthorhombic cell (Table II) shows that the a and b parameters which characterize the plane of the layers do not vary significantly with x . On the contrary, if one observes a plateau for $x < 0.5$, then c decreases significantly as the barium content decreases. Moreover it is worth pointing out that, even for $1 \leq x \leq 1.2$, i.e., in the domain containing impurities, c decreases rather abruptly as x increases. The latter observation suggests that the 2201-phase exists also in this system for a different stoichiometry of the cations. Such a hypothesis is in agreement with a recent single crystal X-ray diffraction study of the 2201 bismuth strontium cuprate (4), which shows that there exists a large strontium deficiency in the studied crystal, bismuth being also partially located in the Sr sites.

The present work demonstrates that $[\text{BaO}]_x$ layers can adopt double $[(\text{Bi})_2]_x$ layers to form an incommensurate structure similar to that of $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ (5), i.e., corresponding to the intergrowth of single octahedral copper layers with triple-distorted rock-salt-type layers.

However, contrary to the lanthanum-substituted phase $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ (6-8), these oxides do not superconduct and are characterized by a high resistivity. Nevertheless, it should be pointed out that the $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ phases exhibit superconductivity for $x < 0.60$ only; unfortunately, it was not possible to obtain the corresponding bismuth barium cuprate for this range of composition. From these observations, it appears that this phase should be considered as a potential superconductor, by taking into account the possibility to intercalate oxygen at high pressure and low temperature using eventually soft chemistry methods. The route to the synthesis of other

members of the series involving barium and bismuth is opened. The study of the second member, involving double copper layers, is in progress.

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