JOURNAL OF SOLID STATE CHEMISTRY 78, 322–325 (1989)

$PbBaYSrCu_3O_8$: A New Member of the Intergrowth Family $(ACuO_{3-x})_m(A'O)_n$

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Communicated by J. M. Honig, December 12, 1988

A new member of the intergrowth family $(ACuO_{3-x})_m(A'O)_n$ has been isolated. $PbBaYSrCu_3O_8$ represents the member $\{m = 3; n = 1\}$. Its structure is formed by stacking $[A'O]_\infty$ single rock-salt-type layers ($A' = Pb, Ba$) and triple oxygen-deficient perovskite layers $[A_3Cu_3O_7]_\infty$ (A = Ba, Pb, Sr, Y). Each perovskite layer for different $m = 3$ members is formed of two pyramidal $[CuO_{2.5}]_\infty$ layers and one $[CuO]_\infty$ layer of corner-sharing CuO_4 square planar group interleaved with Y and Sr ions. The as-synthesized compound is not a superconductor, but evidence of superconductivity at 50 K (less than 1%) is observed by introduction of calcium. A preliminary electron microscopy investigation of this phase shows that it exhibits a modulated structure.

Introduction

The high T_c superconductive copper oxides all belong to the same structural family $(ACuO_{3-x})_m(A'O)_n$ corresponding to the intergrowth of multiple (m) oxygen-deficient perovskite layers and multiple (n) rock-salt-type layers (*1, 2*). Among those oxides, the members $n = 1$, characterized by single rock-salt-type layers, are less numerous. Aside from the well-known La_2CuO_4-type oxides ($m = 1$, $n = 1$) synthesized several years ago (*3*), and the first of the discovered high T_c superconductors (*4*), only the oxide $La_{2-x}A_{1+x}Cu_2O_6$ (A = Ca, Sr) which is not superconducting despite its bidimensional character (*5*) and the superconducting oxide $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$ (*6*) have been reported. We report here on a new member of this family, $PbBaYSrCu_3O_8$, which also contains single rock-salt-type layers, but which differs from the other oxides by the presence of triple oxygen-deficient perovskite layers.

Results and Discussion

The oxide $PbBaYSrCu_3O_8$ was synthesized from a mixture of BaO_2, Sr_2CuO_3, PbO, Y_2O_3, CuO heated at 830°C under a nitrogen flow containing about 1% O_2. The powder X-ray diffraction patterns were indexed in a tetragonal cell with $a = b = 3.842(1)$ Å and $c = 27.66(1)$ Å (Fig. 1). The electron diffraction study of this phase confirmed this tetragonal subcell with $a = b \sim a_p$ and $c \sim 27.7$ Å, with the reflection conditions hkl, $h + k + l = 2n$, leading to the space group $I4/mmm$ (Fig. 2).

However, all the electron diffraction patterns exhibit extra spots whose relative intensity vary from one crystal to the other;

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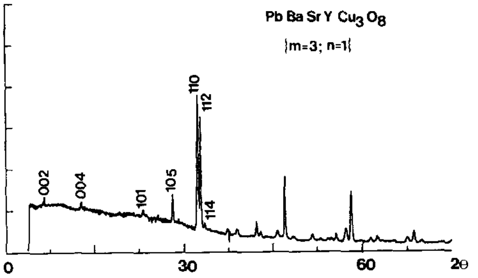

FIG. 1. Powder X-ray diffraction pattern of PbBaYSrCu$_3$O$_8$ (Cu$K\alpha$).

they are particularly visible along a zone slightly deviating from the exact [001] orientation (Fig. 3). These satellites, which look like a two-dimensional modulation, correspond to a complex superposition of two systems characterized by variants oriented at 90°. Both systems are oriented along [110] and [1$\bar{1}$0]. The more intense satellites exhibit a slightly variable wavelength of the modulation, close to four times the d_{110} (2.8 Å); in some crystals, for longer exposure times, satellites in position $\frac{1}{8}$ ($hh0$) are visible (Fig. 3b); moreover, extra spots arise from double diffraction phenomena. The idealized section [001] is reproduced in Fig. 3c; a [1$\bar{1}$0] ED pattern is shown in Fig. 4, where the incommensurate nature of the modulation is clearly visible.

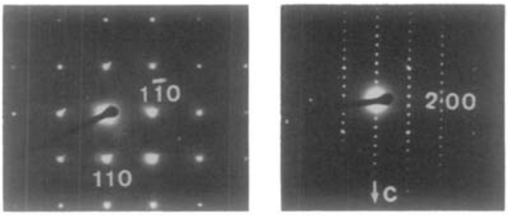

FIG. 2. (001) and (100) electron diffraction patterns of PbBaYSrCu$_3$O$_8$.

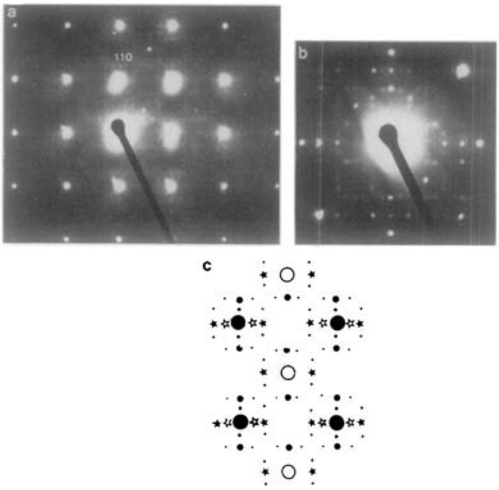

FIG. 3. (a) [001] ED pattern showing extra spots. (b) Spots are clearly visible when the zone is slightly deviated from the exact orientation. (c) Two sets of satellites are visible; they are characteristic of 90° oriented domains. Basic spots at level $\frac{1}{2}$ are represented as open circles. ● ★, Systems 1 and 2 (~4 d_{110}); • ☆, systems 3 and 4 (~8 d_{110}). Small spots, extra spots arising from double diffraction of systems 3 and 4 with 1 and 2 as secondary origins.

From the value of the c parameter and from the space group of the subcell structure, this phase should correspond to the intergrowth of triple perovskite layers with a single rock-salt-type layer (Fig. 5); the compound is labeled 0223. In order to confirm this hypothesis, calculations were performed for PbBaYSrCu$_3$O$_8$ from X-ray powder data on the 35 first reflections, i.e.,

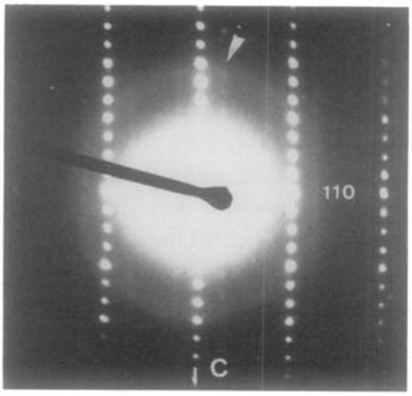

FIG. 4. [1$\bar{1}$0] ED pattern with extra spots in incommensurate positions ($\frac{1}{2}$ l and 4.27 d_{110}).

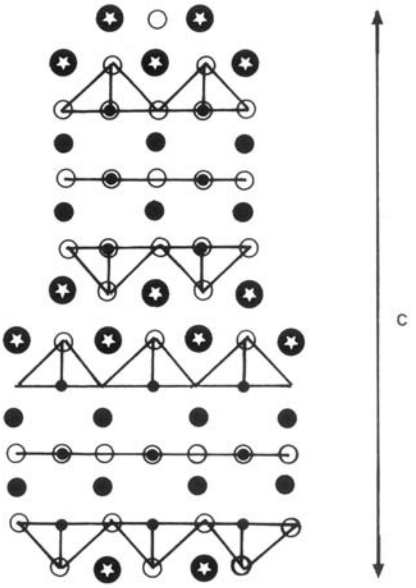

FIG. 5. Idealized drawing of the "0223" structure: $PbBaYSrCu_3O_8$.

48 *hkl* values. Taking into account the problems of modulations and the presence of heavy atoms such as barium and lead it was not attempted to refine the positions of the oxygen atoms denoted O(2), located at the same level as these cations, i.e., in the rock-salt-type layers. Correspondingly, the B factors of all the oxygen atoms were fixed at $B = 1$ Å^2. On the other hand the occupancy factors of the heavier atoms (Ba, Pb, Sr, Y) were refined as well as those of copper.

The discrepancy factor calculated on intensities was lowered to $R = 0.07$ for the atomic coordinates given in Table I. These calculations allow the structural model of this phase to be established without any ambiguity. The structure (Fig. 4) consists of single rock-salt-type layers involving mainly Pb^{2+} and Ba^{2+} cations, and classical triple copper layers built up from two pyramidal $[CuO_{2.5}]_\infty$ layers and one $[CuO_2]_\infty$ layer of square planar groups interleaved with Y^{3+} and Sr^{2+} cations. The occupancy factors observed in Ba/Pb sites of the rock salt layers ($\tau = 0.92$) and in the Y/Sr sites ($\tau = 1.15$) is significant: an occupancy factor $\tau = 1$ in those sites leads to $R = 0.12$. This result is quite compatible with the nominal composition and suggests a partial exchange of lead between the rock salt layers and the perovskite layers according to the following distributions: "$Pb_{0.78}BaSr_{0.22}$" in the rock-salt-type layers and "$Pb_{0.22}Y_1Sr_{0.78}$" in the pseudocubic sites interleaved between the copper layers. The interatomic distances cannot be discussed in detail owing to the lack of accurancy of the results; nevertheless the Cu–O distances (1.92–2.3 Å) as well as the (Y, Sr)–O distances are in agreement with those previously observed for the other compounds of this large family. The (Ba, Pb)–O distances (2.3–3.2 Å) are not as significant, since they are strongly affected by the problems of modulation, which may originate in the rock-salt-type layers. This phenomenon is similar to that observed in bismuth copper (*7–10*) or iron (*11*) oxides for which the satellites have been found to be due to a modulated displacement of the Bi(III) ions and of the oxygen atoms in the rock salt layers (*12, 13*). This modulation can be explained by the stereoactivity of the $6s^2$ lone pair of Bi(III) and Pb(II), which involves a distortion of the octahedra of the rock salt layer.

TABLE I

CRYSTAL DATA OF $PbBaYSrCu_3O_8$: SPACE GROUP *I*4/*mmm*

Atoms	Site	x	y	z	B (Å^2)	τ
PbBa	4e	0	0	0.290 (1)	0.48	0.92
YSr	4e	0	0	0.437 (1)	0.10	1.15
Cu(2)	4e	0	0	0.122 (1)	1.5	1.0
Cu(1)	2a	0	0	0	0.1	1.0
O(1)	4e	0	$\frac{1}{2}$	0	1[a]	1[a]
O(2)	4e	0	0	≈0.2[a]	1[a]	1[a]
O(3)	8g	0	$\frac{1}{2}$	0.118	1[a]	1[a]

[a] These values have been fixed arbitrarily.

Magnetic as well as resistivity measurements so far have not detected any superconductivity in this new phase. Nevertheless, it is now known that the superconducting properties of those phases depend upon the method of synthesis and especially upon the oxygen pressure, so that a more systematic study of the experimental conditions of synthesis must be carried out. However, the substitution of calcium for strontium led to a phase in which approximately 1% diamagnetism was detected at 50 K. This suggests that this system is susceptible to superconductivity determination of its existence range by variation of the cation ratio is in progress.

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