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LETTER TO THE EDITOR

The Oxycarbonate $Y_{1.6}Ca_{0.4}Ba_4Cu_5CO_3O_{11}$, $n = 2$ Member of the "123"-Type Derivatives $(Y_{1-x}Ca_x)_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$

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The exploration of the system Y–Ba–Cu–C–O, using high resolution electron microscopy, has allowed the oxycarbonate $Y_{1.6}Ca_{0.4}Ba_4Cu_5O_{11}CO_3$ to be isolated. This 123 derivative phase is characterized by the superstructure $a \approx 2a_{123}$, $b \approx b_{123}$, $c \approx 2c_{123}$. It corresponds to the ordered replacement of one chain of CuO_4 square planar groups out of two by one row of carbonate groups, involving the formation of chains of CuO_5 pyramids running along **b**. This oxide, which is the first one derived from the pure barium superconductor $Y_{1-x}Ca_xBa_2Cu_3O_7$, can be described as the $n = 2$ member of the 123-type derivatives with the generic formulation $(Y_{1-x}Ca_x)_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$.

Introduction

The possibility of replacing CuO_n polyhedra by carbonate groups in the perovskite structure was demonstrated for the first time by Greaves and Slater (*1*) for the oxycarbonate $Ba_4YCu_{2.27}(CO_3)_{0.53}O_{7.08}$. This study was followed by the synthesis of three other perovskite derivatives, $Sr_2CuCO_3O_2$ (*2*), $(Ba_{1-x}Sr_x)_2Cu_{1+y}(CO_3)_{1-y}O_{2+2y+z}$ (*3*), and $Sr_{1.5}Ba_{0.5}CuCO_3O_2$ (*4*). Recently Miyazaki *et al.* (*5*, *6*) demonstrated that, in the 123 cuprate $YSr_2Cu_3O_7$, 40% of the CuO_4 square planar groups could be replaced by CO_3 groups; moreover, they observed the existence of diffuse superlattice reflections with respect to the classical 123 cell, leading to $2a \times 2c$ and $3a \times 2c$ supercells. The HREM study of this system allowed a well ordered microphase $Y_4Sr_8Cu_{11}CO_3O_{25}$ to be isolated (*7*). The latter, characterized by a $4a \times 2c$ superstructure, resulted from an ordered replacement of one row of CuO_4 square planar groups out of four by a row of CO_3 groups, leaving the oxygen content unchanged with respect to the original O_7 123-structure. Such a substitution would, according to us, be favored by the fact that one oxygen atom of the CO_3 groups forms a CuO_5 pyramid with the CuO_4 square planar group of the adjacent row. Thus, we conceived of the existence of a series of well ordered microphases with the generic formula $Y_nSr_{2n}Cu_{3n-1}CO_3O_{7n-3}$, in which one row of CuO_4 groups out of n is replaced by a row of CO_3 groups, without changing the total oxygen content. Indeed, $Y_4Sr_8Cu_{11}CO_3O_{25}$ corresponds to the $n = 4$ member, whereas the 68-K superconductor $(Y_{1-x}Ca_x)_{0.95}Sr_{2.05}Cu_{2.04}(CO_3)_{0.6}O_y$, recently characterized, with a $2a \times 2c$ superstructure (*8*), represents the $n = 2$ member of the series which would correspond to the ideal formula $Y_{2-x}Ca_{2x}Sr_4Cu_5CO_3O_{11}$; in the same manner, the $3a \times 2c$ superstructure, though it is characterized by diffuse streaks, in the system

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Y–Sr–Cu–C–O (*5*, *6*) would correspond to the composition of the third member of the series, $Y_3Sr_6Cu_8CO_3O_{18}$.

In contrast to strontium cuprate, no substitution of CO_3 for CuO_4 groups has been reported up to now in the 123 superconductor $YBa_2Cu_3O_7$. We have tried to stabilize oxycarbonates in this system by partly replacing yttrium by calcium. The present paper reports on the 123 derivative $Y_{1.6}Ca_{0.4}Ba_4Cu_5CO_3O_{11}$, the second member of the series $(Y_{1-x}Ca_x)_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$.

Experimental

The samples were synthesized from thinly ground mixtures of Y_2O_3, CaO, $BaCO_3$, BaO_2, and CuO, pressed in the form of pellets and sealed in evacuated silica tubes. By varying the proportions of $BaCO_3$ and BaO_2, the partial pressure of O_2 and CO_2 in the tube could be controlled; the samples were heated at 950°C for 14 to 30 h, and the temperature was slowly decreased down to ambient.

Powder X-ray diffraction patterns were registered on a Philips diffractometer with Cu*Kα* radiation. The electron diffraction study was performed with a side entry JEM 200 CX and the high resolution work with a TOPCON 002 B electron microscope equipped with a double tilt sample holder (±10°) and an objective lens with spherical aberration constant $C_s = 0.4$ mm.

The magnetic susceptibility was measured in the temperature range 4–500 K with a SQUID magnetometer Quantum Design.

Results and Discussion

In order to synthesize the $n = 2$ member of the series $(Y_{1-x}Ca_x)_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$, several samples with nominal compositions $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.5}(CO_3)_yO_{6.1+z}$ were prepared, varying the oxygen and CO_2 pressure by changing the $BaCO_3/BaO_2$ ratio with $0.5 \leq y < 1$.

The powder X-ray diffraction analysis shows that an almost pure 123-phase can be synthesized for y and z values in the above range of composition; only traces of $BaCO_3$ are detected.

The electron diffraction patterns of these different samples all exhibit the fundamental reflections characteristic of the 123 structure, but extra reflections are always observed. The construction of the reciprocal space provides evidence for an orthorhombic supercell with $a \approx 2a_{123}$, $b \approx b_{123}$, and $c \approx 2c_{123}$, with the reflection conditions hkl $(h + l = 2n)$ leading to the possible space groups *B*222, *Bm*2*m*, and *Bmmm* (Fig. 1).

Although they are weak (i.e., less than 2% of the intensity of the 103 reflections), extra reflections are observed on the XRD Guinier films, which can be indexed in the above supercell. The refined parameters of the corresponding 123 subcell $a = 3.8903$ (3) Å, $b = 3.8427$ (3) Å, and $c = 11.621$ (1)

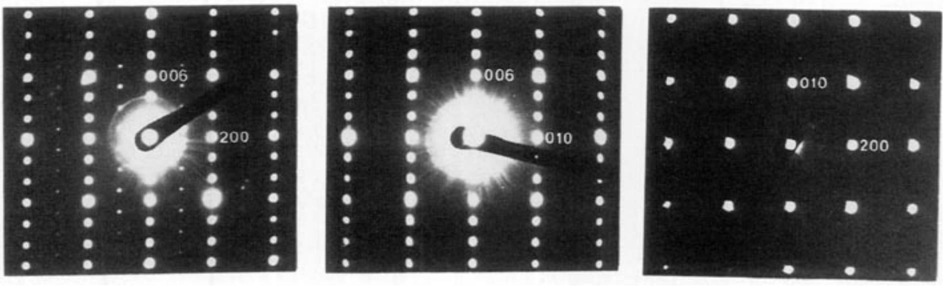

FIG. 1. Characteristic electron diffraction patterns of $(Y_{0.8}Ca_{0.2})Ba_2Cu_{2.5}(CO_3)_yO_{6.1+z}$ samples showing the reflection existence conditions $h0l$ $h + l = 2n$, $0kl$ $l = 2n$, $hk0$ $h = 2n$.

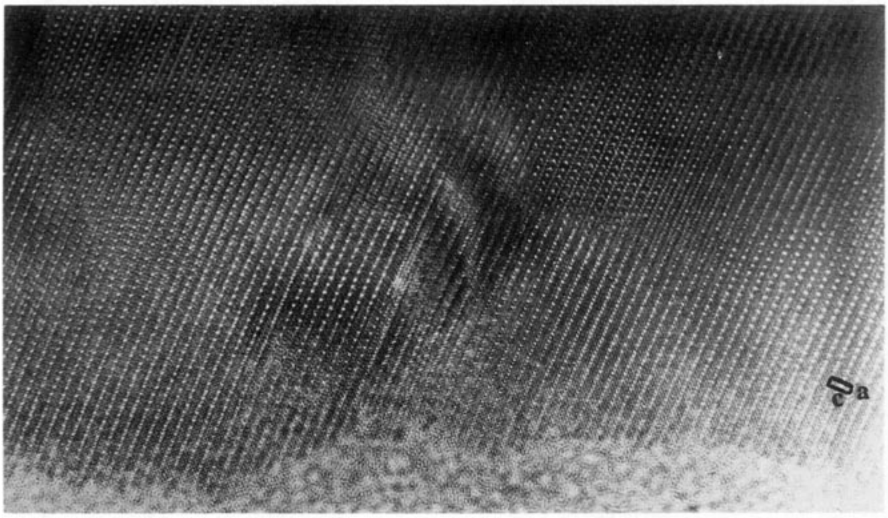

FIG. 2. Characteristic [010] HREM image of $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.5}(CO_3)_{0.5}O_{6.1+z}$ microcrystal showing the regular distribution over the whole matrix of bright dots associated, for −15 nm focus value, to C atoms of CO_3 groups substituted for CuO_4 square planes, which form a $2a_{123} \times 2c_{123}$ centered array.

Å show that c is significantly smaller than for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_7$ (11.69 Å).

These results, and especially the existence of a $2a \times 2c$ superstructure similar to that observed in the Y–Ca–Sr–Cu–Cr–O system (*8*), suggest that this phase corresponds to the oxycarbonate $(Y_{0.8}Ca_{0.2})_2Ba_4Cu_5CO_3O_{11}$ whose structure would result from the ordered replacement of one chain of CuO_4 groups out of two by a row of CO_3 groups.

To confirm this structural model, a HREM investigation was performed. As previously mentioned (*7*), the suitable orientation for such a characterization is along [010]. The [010] experimental images of many crystals show a contrast typical of carbonated samples. The image of Fig. 2, taken with a focus close to −15 nm, was found to be very sensitive to the presence of CO_3 groups in our previous study of the Y–Sr oxycarbonate (*7*). On the thin edge of the crystal one observes a contrast very similar to that in $Y_4Sr_8Cu_{11}CO_3O_{25}$, but the lighter dots, related to the CO_3 groups, here form a $2a_{123} \times 2c_{123}$ centered array, instead of a $4a_{123} \times 2c_{123}$ array. Moreover, this contrast periodicity is also observed in the thicker part of the crystal.

These observations demonstrate that this new phase corresponds to the ordered substitution of one row out of two of CO_3 groups for a $[CuO_2]_\infty$ chain of square plane out of two in the Cu1 layer of the $YBa_2Cu_3O_7$ structure, and that this arrangement is shifted by $a/2$ in the adjacent layer (Fig. 3). Note that this ordered substitution of the CuO_4 groups by CO_3 groups leads to the formation of CuO_5 pyramids: at the level of Cu1 atoms, this structure is described as chains of CuO_5 pyramids running along **b** and linked through triangular CO_3 groups.

In identical samples, heated for several hours and quenched from 950°C down to room temperature, the extra reflections disappeared both from powder XRD patterns and on the ED patterns, contrary to those quenched after a week's heating. Thus the synthesis conditions play an important role in the ordering of the carbonate groups in this structure.

These results suggest that n other members of this series, corresponding to various superstructures, should exist. For this rea-

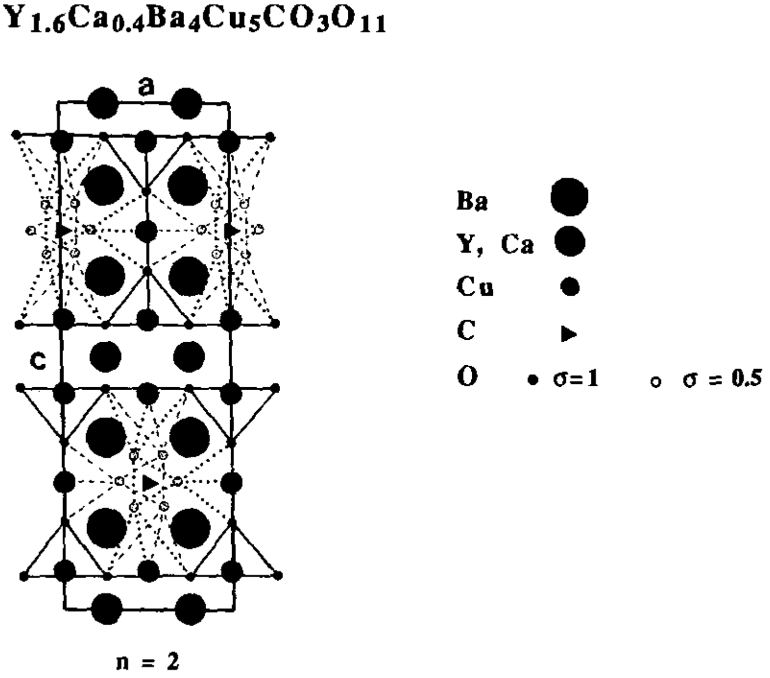

FIG. 3. [010] projection of idealized structure of the $n = 2$ member of $(Y_{1-x}Ca_x)Ba_{2n}Cu_{3n-1}CO_3O_{7n-3}$ series.

son attempts were made to prepare other members with $n > 2$, starting from the nominal compositions $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-w}(CO_3)_w O_{6+z}$, with $0.10 < w \leq 0.5$. Under the above experimental conditions we always observed the same superstructure $2a_{123} \times b_{123} \times 2c_{123}$. However, the ED patterns show that the intensity of the extra reflections varies from one sample to the other. These variations are correlated to the existence of more or less extended, well ordered $2a_{123} \times 2c_{123}$ domains. An example of such a domain is shown on the [010] image of a sample of nominal composition $w = 0.16$ (Fig. 4). The superstructure correlated to the 1–1 ordering of the rows of CuO_4 and CO_3 groups is clearly visible in domain ① (lower right side); it is also detected in a noncarbonated classical $YBa_2Cu_3O_7$-type (domain ②) matrix, as attested by the through focus images. Nevertheless, the presence of isolated CO_3 groups in the 123 matrix is also most probable. Thus, the variation of the CO_3 content in the $YBa_2Cu_3O_7$-type matrix probably appears in the form of $Y_{1.6}Ca_{0.4}Ba_4Cu_5CO_3O_{11}$-type domains (type ①) coherently distributed in the matrix. Variations of the experimental conditions at higher temperatures and different compositions (Y/Ca ratio, CO_2 and O_2 pressure) will be necessary in attempts to stabilize the other ordered members of the series for this system.

Magnetic susceptibility measurements on different samples with nominal compositions $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.5}(CO_3)_yO_{6+y}$ did not provide any evidence for superconductivity, whereas those performed on the reference noncarbonated phase $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (prepared with the same procedure) confirmed the superconducting properties of this cuprate; the T_c value of 80 K is in agreement with previous studies (*9*). This result demonstrates the negative influence of carbonate groups on superconductivity for this compound. Nevertheless,

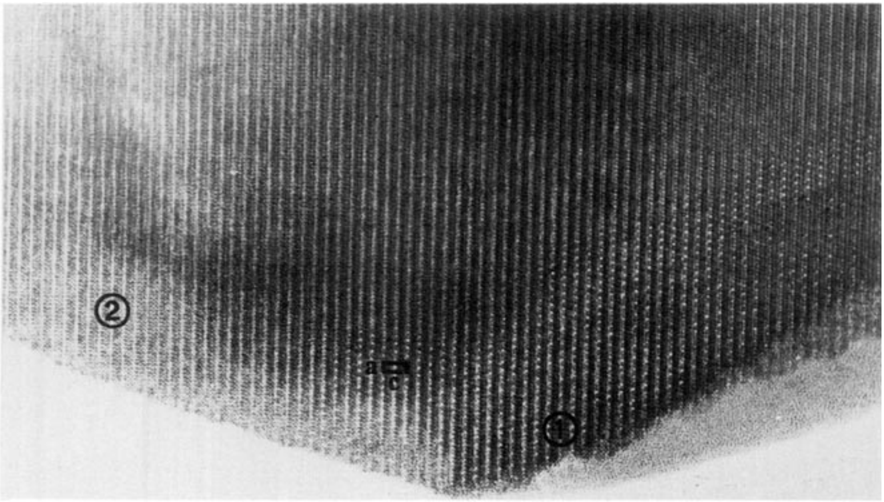

FIG. 4. Characteristic [010] HREM image of a $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.84}(CO_3)_{0.16}O_{6+2}$ microcrystal showing two types of domains: ① $Y_{1.6}Ca_{0.4}Ba_4Cu_5(CO_3)O_4$-type with fairly well established "$2a_{123} \times 2c_{123}$" superstructure; ② (Y, Ca)Ba_2O_7-type area without any observable superstructure.

from the charge balance viewpoint, a partial oxidation of copper remains possible. Thus, a careful study of annealing conditions—time, temperature, pressure—is required to understand the mechanisms of superconductivity in these phases.

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