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Substitution of "CO_3" Groups for Copper in YBCO: The Oxycarbonates $Y_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$

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The substitution of carbonate groups for copper in the oxide $YBa_2Cu_3O_7$ has been studied by HREM. Two new phases, members of the series $Y_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$ have been evidenced for $n = 2$ and 3, respectively. The corresponding superstructures "$2a_{123}\times b_{123}\times 2c_{123}$" and "$3a_{123}\times b_{123}\times 2c_{123}$" correspond to the ordered substitution of one row of CO_3 groups for one row of CuO_4 groups out of two and three, respectively. The existence of 90°-oriented domains and of chemical twinning is also shown and the role of CO_3 groups at the domain boundaries discussed.

Introduction

The recent investigations of the substitution of the carbonate groups for copper in the **123** structure have allowed new phases with the formula $(Y_{1-x}Ca_x)_nA_{2n}Cu_{3n-1}CO_3O_{7n-3}$[1-6] to be evidenced for A = Sr, Ba. Some of these phases were found to superconduct, but with a critical temperature significantly smaller than that of the 92 K superconductor $YBa_2Cu_3O_7$. The possibility of introducing CO_3 groups into the **123** structure, known to occur for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$,[5,6] has never been studied up to now for the pure barium cuprate $YBa_2Cu_3O_7$. Such an investigation is absolutely necessary if one takes into consideration the large possibility of applications of this material, which is now prepared and used either in the form of textured ceramics or of thin films. Carbonation phenomena might then appear at the level of CuO_4 square planes of the structure, depending on the experimental method used for the process, that would alter the superconductivity of the films or ceramics. The present paper reports on the electron microscopic observations of oxycarbonates that were obtained from samples with nominal composition $Y_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$.

Experimental Section

The samples were synthesised from mixtures of Y_2O_3, $BaCO_3$, BaO_2, $BaCuO_2$, and CuO following the formulation $Y_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$, ground together in an agate mortar, pressed into pellets and sealed in evacuated silica tubes, the CO_2 partial pressure being varied by changing the $BaCO_3/BaO_2/BaCuO_2$ ratios. Thus, the following molar ratios of Y_2O_3, $BaCO_3$, BaO_2, $BaCuO_2$, and CuO were used to make the $n = 2$, 3, and 6 compounds respectively: [1:1:0:3:2], [1.5:1:0.5:4.5:3.5], and [3:1:2:9:8]. Samples were heated at 800 or 900 °C for 6 h to 15 days, and the temperature was slowly decreased to ambient. Within the temperature and time limits given—i.e., a typical procedure would be heating the tube at 800 °C for 48 h before a 60 °C/h decrease in temperature—these synthesis conditions allow the stabilization of a **123**-based oxycarbonate as major phase. Nevertheless, as detailed further, the observed n values do not always correspond to the initial composition.

Powder X-ray diffraction patterns were registered on a Philips diffractometer, with Cu Kα radiation equipped with a backface monochromator. The electron diffraction study was performed with a JEOL 200CX electron microscope fitted with an eucentric goniometer (±60°) and the high-resolution work with a TOPCON 002B microscope equipped with a double-tilt sample holder (±10°) and an objective lens with spherical aberration constant $C_s = 0.4$ mm. For electron microscopy study, samples were gently ground in n-butanol and deposited on a holey carbon coated aluminum grid.

Results and Discussion

Whatever the nominal composition $n = 2$, 3, or 6 may be, i.e., whatever the CO_2 pressure, the powder X-ray diffraction pattern does not vary significantly. It evidences a 123-type major phase, Y_2BaCuO_5, and $BaCO_3$ as a secondary phase. Nevertheless, if they do not vary, the refined parameters of the corresponding orthorhombic cell are different from those of $YBa_2Cu_3O_7$:

$$a = 3.857(1)\ \text{Å},\quad b = 3.885(1)\ \text{Å},\quad c = 11.585(1)\ \text{Å}$$

One indeed observes a significant decrease of the c parameter with respect to $YBa_2Cu_3O_7$ ($c = 11.676$ Å) leading to $c/a = 3.00$ and $c/b = 2.98$. These preliminary results suggest a partial replacement of CuO_4 groups by "CO_3" groups; however, one does not observe any extra reflections that could imply an ordering of the rows of square-planar groups and of carbonate groups.

The electron diffraction patterns are all characterized by the superimposition of 90°-oriented domains, as shown from the intense reflections in Figure 1. Their complexity is easily explained by the equivalent values of the a_p parameter along the three directions of the perovskite subcell, so that the three zone axes [100], [010], and [001]

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(1) Miyazaki, Y.; Yamane, H.; Ohnishi, N.; Kajitani, T.; Hiraga, K.; Morii, Y.; Funahashi, S.; Hirai, T. *Physica C* **1992**, *198*, 7.

(2) Domengès, B.; Hervieu, M.; Raveau, B. *Physica C* **1993**, *207*, 65.

(3) Ohnishi, N.; Miyazaki, Y.; Yamane, H.; Kajitani, T.; Hirai, T.; Hiraga, K. *Physica C* **1993**, *207*, 175.

(4) Akimitsu, J.; Uehara, M.; Ogawa, M.; Nakata, H.; Tomimoto, K.; Miyazaki, Y.; Yamane, H.; Hirai, T.; Kinoshita, K.; Matsui, Y. *Physica C* **1992**, *201*, 320.

(5) Hervieu, M.; Boullay, Ph.; Domengès, B.; Maignan, A.; Raveau, B. *J. Solid State Chem.* **1993**, *105*, 300.

(6) Domengès, B.; Boullay, Ph.; Hervieu, M.; Raveau, B. *J. Solid State Chem.*, in press.

(7) Wiles, D. B.; Young, R. A. *J. Appl. Crystallogr.* **1981**, *14*, 149.

0897-4756/93/2805-1683$04.00/0

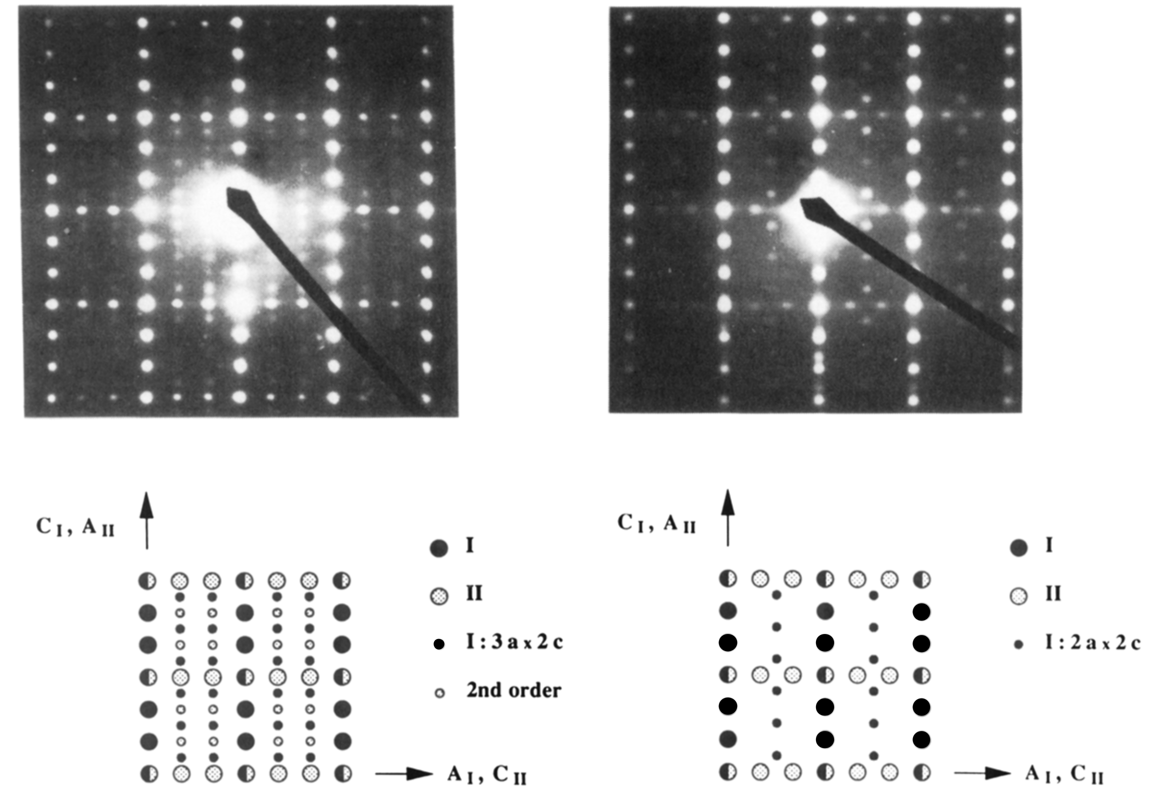

Figure 1. [010] ED patterns of (a, left) $n = 3$ and (b, right) $n = 2$ microcrystals showing two superimposed 90° oriented lattices. In (a) observed satellites in **I** lattice lead to the superlattice $\sim 3a\times 2c$, whereas in (b) satellites lead to a centered $2a\times 2c$ lattice.

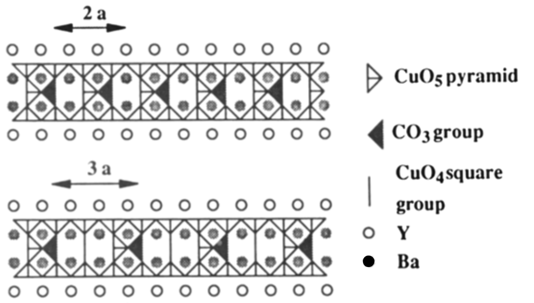

Figure 2. [010] projection showing the regular substitution of carbonate groups for CuO_4 groups leading to a doubling of the a parameter in $Y_2Ba_4Cu_5CO_3O_{11}$ and a tripling of the a parameter in $Y_3Ba_6Cu_8CO_3O_{18}$.

can be observed simultaneously on the same pattern. For most of the crystals one observes satellites, but their intensity varies dramatically from one crystal to the other. The $n = 3$ and $n = 2$ samples exhibit different superstructures. The ED patterns of the first one (Figure 1a) show incommensurate satellites corresponding to the supercell $a \approx q\times a_{123}$, $b \approx b_{123}$, $c \approx 2c_{123}$ with q close to 3, whereas for the second one the observed satellites (Figure 1b) correspond to a B centered supercell $a \approx 2a_{123}$, $b \approx b_{123}$, $c \approx 2c_{123}$. For $n = 6$, incommensurate satellites of the first type could only be observed. These observations support the viewpoint that in these samples the rows of CuO_4 square planar groups are replaced by rows of CO_3 groups in an ordered way, as in the Sr-based 123 oxycarbonates.[3] The doubling of the "a" parameter of the $n = 2$ sample suggests that one row of carbonate group is substituted for one row of CuO_4 groups out of two forming rows of CuO_4 pyramids at the level of Cu1 (Figure 2), in agreement with the nominal composition $Y_2Ba_4Cu_5CO_3O_{11}$; the tripling of the "a" parameter, which corresponds to a substitution of one row of CO_3 groups for one row of CuO_4 group out of three in the $n = 3$ sample, follows the nominal composition $Y_3Ba_6Cu_8CO_3O_{18}$.

In agreement with the ED results, the high-resolution electron microscopy study leads to two main conclusions: all the observed crystals show domains and a contrast characteristic of carbonated **123** compounds, the density of carbonate substitution being directly correlated to the satellite intensity. As mentioned for other **123** oxycarbonates, one of the most favorable focus value is 10 nm to enhance the carbonate substitution for copper. On the 10-nm image of an $n = 3$ sample $Y_3Ba_6Cu_8CO_3O_{18}$ microcrystal (Figure 3a), the 0.38-nm spaced bright dots forming rows parallel to $\vec{a}$ can be correlated to mixed carbon/copper sites of the structure. Indeed, it has been shown[6] that for this focus value, cation rows appear as bright spots: for thin specimens ($\sim$3 nm), three rows of brighter spots, corresponding to barium and mixed copper–carbon rows, alternate with three rows of a grayer ones, corresponding to yttrium and pyramidal copper rows; for thicker specimens ($\geq$5 nm), only the mixed copper–carbon rows are highlighted. On the latter rows, carbon appears as brighter dots. Thus, the ordering of carbonate can be directly related to the contrast modulation. In Figure 3, an almost regular $n = 3$ area is observed, where one of every three copper atoms is substituted by carbon. On the upper part of the image, the ordered replacement of one carbon every three copper of the CuO_4 square plane leads to a monoclinic elementary unit, $3a_m$-type unit. Thus, the $3a_I$- (upper part of the image) and $3a_{II}$-type units introduced by Ohnishi's et al.[3] can be deduced from this monoclinic elementary unit by a simple chemical twinning (Figure 3).

The substitution of carbonate groups for CuO_4 groups never follows a true regular arrangement and no satellite system has ever been observed leading to a true monoclinic

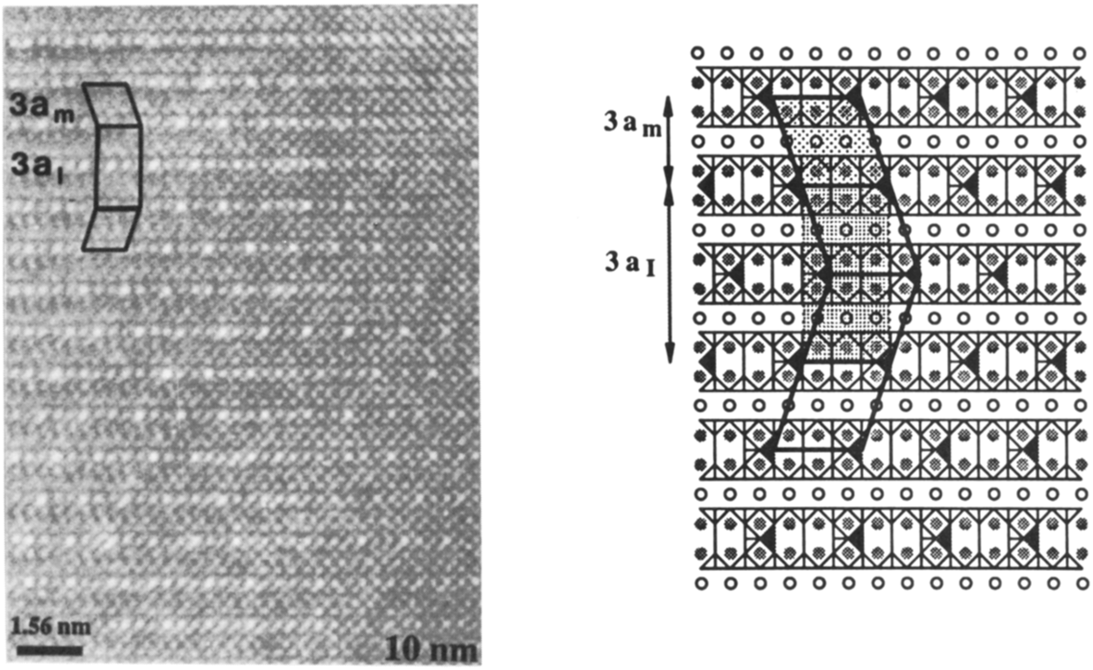

Figure 3. [010] HREM image of an $Y_3Ba_6Cu_8CO_3O_{18}$ microcrystal taken for a focus close to 10 nm. Brighter dots are correlated to carbon atoms. The corresponding [010] projection of an $n = 3$ regular area allows to define a monoclinic elementary $3a_m$ unit which leads by chemical twinning to the orthorhombic $3a_I$ unit.

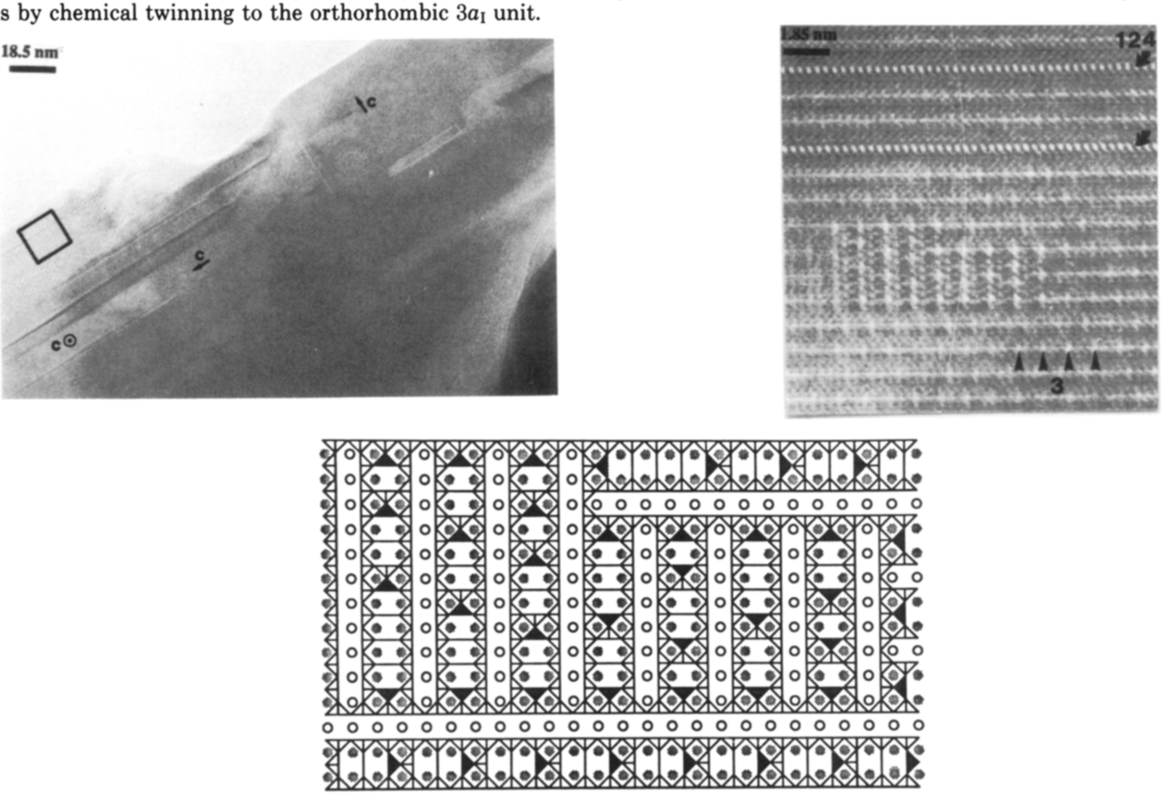

Figure 4. (a, left) Low-magnification HREM image showing a mosaic-like contrast based on 90° rotated domains. (b, bottom) Detail showing that domain boundaries are carbon rich as proposed on joined model. Two defective **124** slabs are also observed (curved arrows).

symmetry. Nevertheless the EM observations suggest a pseudoperiodic replacement corresponding to values of n close to 3 or 2. The peculiarity of the carbonated Ba-based **123** samples is shown on Figure 4. The size of 90° oriented domains is very small compared to that of other **123** oxycarbonates and images show a mosaic-like contrast (Figure 4a). A detailed view (Figure 4b) confirms that the substitution of carbonate groups for CuO_4 groups at the level of Cu(1) has occurred almost periodically one time out of three. Note, similar to previous observations in carbonated Ca-based **123** samples, the smooth transition between 90° rotated domains that may be achieved through CO_3 groups (Figure 4). Furthermore, the boundary between the 90° rotated domains follows steps parallel to $(001)_{123}$ as on Figure 5 where the domain junction forms a complex steplike path highlighted with bright dots corresponding to CO_3 groups.

Conclusion

The introduction of carbonate groups on the copper

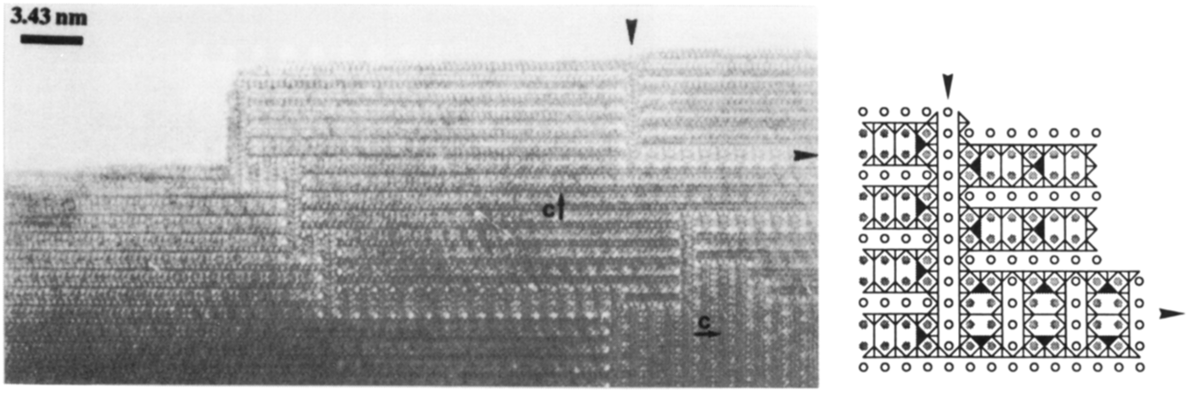

Figure 5. HREM image and corresponding model of a microcrystal showing that the domain boundary follows steps parallel to $(001)_{123}$.

sites of $YBa_2Cu_3O_7$ has been demonstrated, leading to two ordered members, $n = 2$ and $n = 3$, of the family $Y_nBa_{2n}Cu_{3n-1}CO_3O_{7n-3}$. Attempts to prepare $YBa_2Cu_3O_7$, in a sealed ampule starting from BaO_2, have always evidenced the formation of these oxycarbonates. Moreover, prepared under the experimental conditions described above, none of the Ba-based **123** oxycarbonates superconduct. It is now clear from this study that the formation of such oxycarbonates depends on the experimental conditions, so that possible carbonation phenomena that may alter the superconducting properties should be taken into consideration for particular experimental methods used during the process of ceramics or of thin films. Electron microscopy can be used as a tool to identify the presence of such carbonates in the final material.