JOURNAL OF SOLID STATE CHEMISTRY **103**, 533–538 (1993)

Structural Changes Accompanying the Low-Temperature Annealing of $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$): Transformation of the 123 Phase to a 124-Type Structure*

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Communicated by J. M. Honig, February 9, 1993

Superconducting $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$) compositions seem to transform to a metastable $YBa_2Cu_4O_8$ (124)-like phase with a *c* parameter of 27.2 Å on annealing at 473 K for a few hours.

Based on electron microscopy and other studies, $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$) compositions with a superconducting transition temperature of ~60 K (in the plateau region of the T_c–δ plot) have been shown to be thermodynamically metastable, disproportionating into more-stable phases on annealing at relatively low temperatures (~470 K) for a few hours (*1, 2*). These 123 compositions have an orthorhombic structure distinctly different from that of compositions with $\delta \leq 0.25$ (T_c ~90 K), where the *c* lattice parameter is exactly three times the *b* parameter. A significant feature of the effect of annealing $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$) compositions at 470 K is the marked change in the X-ray diffraction pattern occurring after a period of ~48 hr. This is accompanied by streaking in the electron diffraction pattern along the c^* direction, indicating considerable oxygen disorder in the *ab* plane. We were interested in investigating the nature of the structural transformation occurring in $YBa_2Cu_3O_{7-\delta}$ when subjected to low-temperature annealing and have therefore carried out a systematic study of the effect of annealing several compositions of $YBa_2Cu_3O_{7-\delta}$ (δ = 0.50, 0.43, 0.34, 0.29, 0.22, and 0.08) in different atmospheres at 473 and 573 K.

All the $YBa_2Cu_3O_{7-\delta}$ compositions except the one with $\delta = 0.08$ are oxidized to $YBa_2Cu_3O_{6.92}$ when heated in air at 573 K or in oxygen at 473 K. When the samples were heated in air or in dynamic vacuum (~10^{-3} torr) at 473 K, there was no significant change in the δ = 0.50 and 0.08 compositions. However, changes signifying the formation of new phases, accompanied by a low-angle reflection of $2\theta \sim 6.5$–6.7°, occurred in compositions with δ values of 0.43, 0.34, 0.29, and 0.22. In Table I, we summarize the information on the gross changes occurring on low-temperature annealing of $YBa_2Cu_3O_{7-\delta}$ compositions.

In Fig. 1 we show the X-ray diffraction patterns of $YBa_2Cu_3O_{6.7}$ subjected to annealing for different periods at 473 K in air. New features, especially the low-angle reflection, begin to emerge on annealing the

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0022-4596/93 $5.00

TABLE I

CHANGES OCCURRING IN $YBa_2Cu_3O_{7-\delta}$ ON ANNEALING

δ	Structure after heating at 473 K (48 hr) in			Structure after heating at 573 K (48 hr) in air
	Vacuum	Air	O_2	
0.50	No change	No change	Oxidizes to $YBa_2Cu_3O_{6.92}$	Oxidizes to $YBa_2Cu_3O_{6.92}$
0.43	Changes to new phase(s)	Changes to new phase(s)	Oxidizes to $YBa_2Cu_3O_{6.92}$	Oxidizes to $YBa_2Cu_3O_{6.92}$
0.34	Changes to new phase(s)	Changes to new phase(s)	Oxidizes to $YBa_2Cu_3O_{6.92}$	Oxidizes to $YBa_2Cu_3O_{6.92}$
0.29	Changes to new phase(s)	Changes to new phase(s)	Oxidizes to $YBa_2Cu_3O_{6.92}$	Oxidizes to $YBa_2Cu_3O_{6.92}$
0.22	Changes to new phase(s)	Changes to new phase(s)	Oxidizes to $YBa_2Cu_3O_{6.92}$	Oxidizes to $YBa_2Cu_3O_{6.92}$
0.08	No change	No change	No change	No change

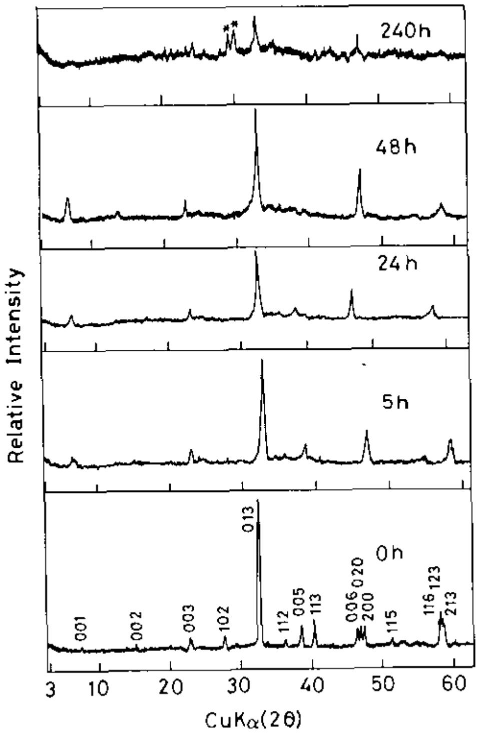

FIG. 1. Changes occurring in the X-ray diffraction pattern of $YBa_2Cu_3O_{6.7}$ annealed at 473 K in air for different periods.

sample for 24 hr. After 240 hr of heating, however, the material starts to decompose into $BaCuO_2$ and other phases. Changes similar to those in Fig. 1 are also found on annealing other compositions of $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$). We notice from Fig. 1 that the X-ray lines become broad on annealing for 48 hr, indicating extensive disorder. The X-ray diffraction pattern therefore appears more like that of a tetragonal cuprate than that of an orthorhombic cuprate. The low-angle line around $2\theta \sim 6.6°$ corresponds to a c parameter of 27.2 Å. Furthermore, the position of the low-angle reflection varies proportionally with the c parameter of the starting $YBa_2Cu_3O_{7-\delta}$ composition. It is noteworthy that the c parameter of 27.2 Å is close to that of $YBa_2Cu_4O_8$ (124 phase) and that the corresponding 004 reflection is also present in the diffraction pattern of the annealed product (see Fig. 1).

The low-angle X-ray reflection at $2\theta \sim 6.6$ Å appears in all the $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$) compositions after annealing at 473 K, suggesting that all these oxygen-deficient 123 compositions may be transforming to $YBa_2Cu_4O_8$. Such a transformation of $YBa_2Cu_3O_{7-\delta}$($\delta = 0.25$), yielding $YBa_2Cu_4O_8$ together with Y_2BaCuO_5 and

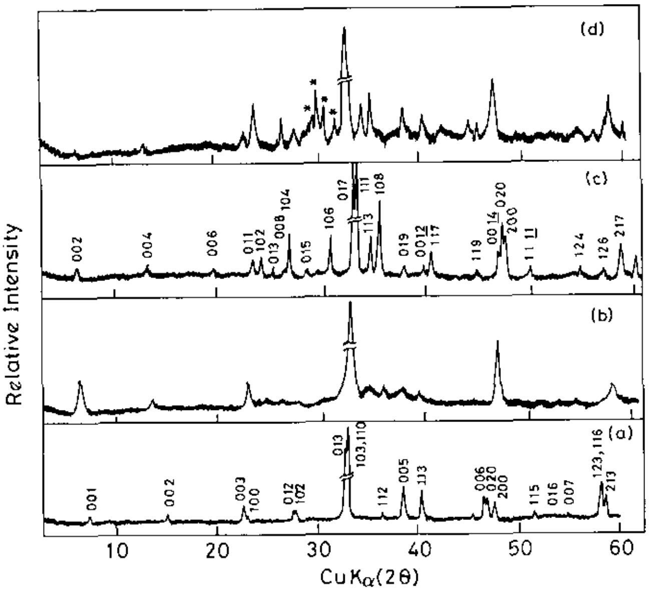

FIG. 2. Powder X-ray diffraction patterns of (a) $YBa_2Cu_3O_{6.7}$, (b) the product obtained after $YBa_2Cu_3O_{6.7}$ is annealed at 473 K in air for 48 hr, (c) bulk $YBa_2Cu_4O_8$ (*Ammm*), (d) a mixture of $YBa_2Cu_4O_8$ (*Ammm*) and $YBa_2Cu_{2.7}O_x$ containing $BaCuO_2$ and Y_2BaCuO_5.

$BaCuO_2$, has been considered in the literature [3]:

$$4\ YBa_2Cu_3O_{6.75} \rightarrow 2\ YBa_2Cu_4O_8 + Y_2BaCuO_5 + 3\ BaCuO_2.$$

This transformation is expected to be feasible at or below 873 K at an oxygen pressure of one atmosphere. An examination of the X-ray diffraction pattern of $YBa_2Cu_3O_{6.7}$ heated at ~473 K in air for 48 hr (Fig. 1) shows that there is no obvious presence of $BaCuO_2$ and other impurity phases; these appear only after extensive heating (~240 hr). The X-ray diffraction pattern of the product obtained after annealing for 48 hr in air is indeed much too simple and does not appear to be like the pattern of bulk $YBa_2Cu_4O_8$ (*Ammm* space group) or of a mixture of $YBa_2Cu_4O_8$ with Cu-deficient $YBa_2Cu_3O_{7-\delta}$, $BaCuO_2$, etc. (Fig. 2). Neither could we reconcile the observed pattern with that of $Y_2Ba_4Cu_7O_{15}$ (247 phase) or any other intergrowth between 124 and 123 phases. Cu-deficient 123 cuprates of the type $YBa_2Cu_{3-x}O_{7-\delta}$ cannot be prepared in pure form for $x > 0.2$. When $x > 0.2$, the cuprate prepared by the ceramic method contains $BaCuO_2$ and other impurities.

There is some electron microscopic evidence for the transformation of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$, as well as of some other rare earth 123 cuprates, into 124 (Y (*Ln*) $Ba_2Cu_4O_8$) phases, without giving rise to other copper oxide phases (*4*). Such a transformation appears to be favored by planar defects along the *c* axis associated with oxygen disorder. Furthermore, HREM images show that the 124 slabs extend over considerable regions of the crystals. As mentioned earlier, the X-ray diffraction pattern of $YBa_2Cu_3O_{6.7}$ annealed at 473 K for 48 hr (Fig. 2b) does not correspond to that of bulk $YBa_2Cu_4O_8$(*Ammm*), as can be seen from Fig. 2c. We see no evidence for the formation of cuprates of the type $YBa_2Cu_5O_{10}$. We can, however, conceive of metastable forms of $YBa_2Cu_4O_8$ involving *I*-centering or primitive-centering instead of the *A*-centering present in bulk $YBa_2Cu_4O_8$ (*Ammm*) prepared in the laboratory. The

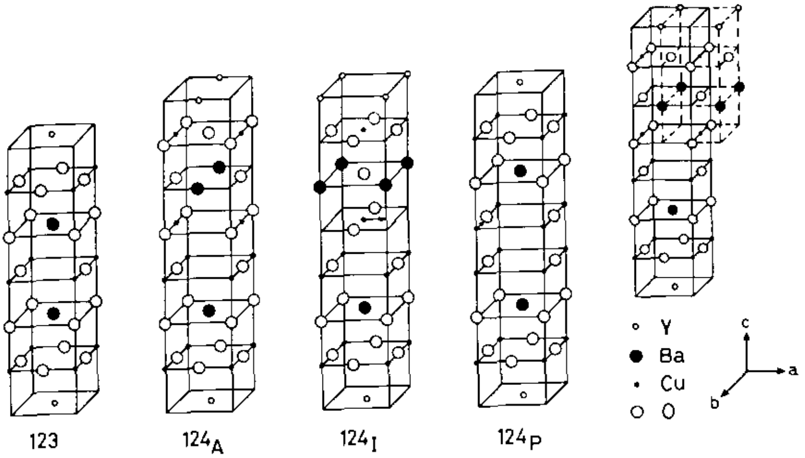

FIG. 3. Unit cells of $YBa_2Cu_3O_7$ along with the A-centered, I-centered, and P-centered forms of $YBa_2Cu_4O_8$. Inset shows the shear mechanism involved in the transformation from A-centered to I-centered $YBa_2Cu_4O_8$.

I-centered and P-centered $YBa_2Cu_4O_8$ structures can be generated from the $YBa_2Cu_4O_8$ (*Ammm*) structure (*4*) by a shear operation of half of the unit cell by $a/2$ or $b/2$, respectively (Fig. 3). Both the I-centered and P-centered structures of $YBa_2Cu_4O_8$ would involve two copper atoms with an unfavorable threefold coordination of oxygen, whereas in $YBa_2Cu_4O_8$ (*Ammm*), the chain copper atoms have aplanar fourfold coordination of oxygen. The I- and P-centered structures are therefore

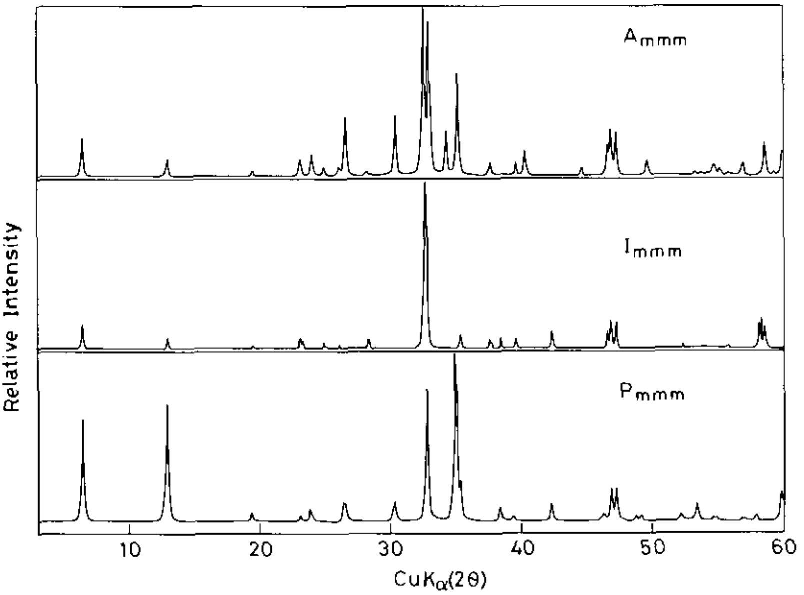

FIG. 4. Computed X-ray diffraction patterns of $YBa_2Cu_4O_8$ in *Ammm*, *Immm*, and *Pmmm* space groups for the same c parameter (27.24 Å).

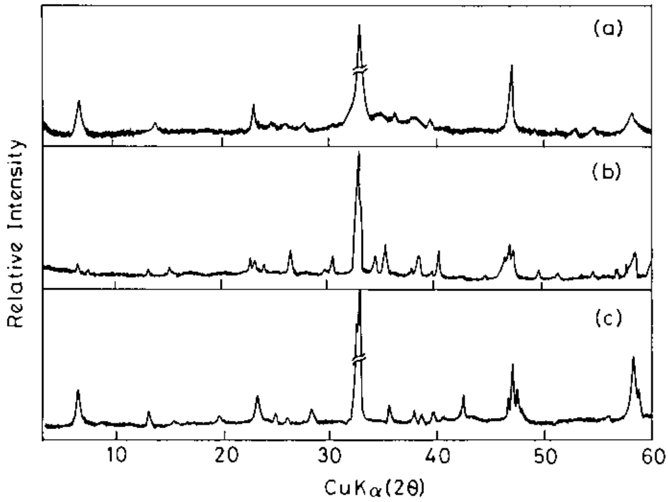

FIG. 5. Comparison of the X-ray diffraction patterns of (a) the product obtained after annealing $YBa_2Cu_3O_{6.7}$ at 473 K for 48 hr in air with the patterns of (b) 80 : 20 mixture of $YBa_2Cu_4O_8$ (*Ammm*) and $YBa_2Cu_3O_{6.7}$ and (c) 80 : 20 mixture of $YBa_2Cu_4O_8$ (*Immm*) and $YBa_2Cu_3O_{6.7}$.

unlikely to be stable phases which can be synthesized by the usual methods, but which are formed as metastable phases during the course of the transformation of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$.

In order to assign the structure of the product obtained by annealing $YBa_2Cu_3O_{6.7}$ at 473 K for 48 hr, we computed the X-ray diffraction patterns of $YBa_2Cu_4O_8$ in the *I*- and *P*-centered forms, taking into consideration the highest symmetry elements of the point group, *mmm*, as well as the lattice parameters of $YBa_2Cu_4O_8$ (*Ammm*). The computed diffraction patterns are shown in Fig. 4. The experimentally observed diffraction pattern of the product, obtained after annealing $YBa_2Cu_3O_{6.7}$ at 473 K in air for 48 hr, seems to be definitely closer to that of the *Immm* form of $YBa_2Cu_4O_8$. Since some untransformed $YBa_2Cu_3O_{6.7}$ is always present after the annealing for 48 hr, we have compared the observed X-ray diffraction pattern of the transformed product (Fig. 5a) with that of a 80 : 20 mixture of the $YBa_2Cu_4O_8$ (*Ammm*) phase with $YBa_2Cu_3O_{6.7}$ (Fig. 5b). The correspondence is not as good as that with the computed pattern of a 80 : 20 mixture of $YBa_2Cu_4O_8$ (*Immm*) with $YBa_2Cu_3O_{6.7}$. We believe that the structural transformation $YBa_2Cu_3O_{6.7}$ to the 124 phase is aided by the oxygen disorder (in the *ab* plane) inherently present in the starting cuprate composition. Oxygen vacancies in $YBa_2Cu_3O_{7-\delta}$ ($0.3 \leq \delta \leq 0.4$) are not ordered sufficiently to give rise to a well-defined defect structure as in $YBa_2Cu_3O_{6.5}$ (*1, 2, 5–7*). The metastability of the 124(*Immm*) with the unusual coordination of chain Cu atoms is likely to be responsible for its decomposition to $BaCuO_2$ and other phases on long annealing. Furthermore, the rather broad X-ray reflections resulting from disorder in the product of low-temperature annealing of $YBa_2Cu_3O_7$ (see Fig. 1 or 2b) masks the orthorhombicity, if any, and the structure appears to be tetragonal. An *I4/mmm* space group would indeed make the diffraction pattern even simpler than that of the *Immm* structure shown in Figs. 4 and 5.

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