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Two phase co-existence in $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ superconductor with x = 0.03

X. S. WU, F. M. PAN, X. R. HUANG, C. YE, X. JIN, S. S. JIANG
National Laboratory of Solid State Microstructures, Centre for Advanced Studies in Science and Technology of Microstructures, Department of Physics, Nanjing University, Nanjing 210093, Peoples Republic of China

Co-doped impurity-free $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$($123Co_x$) with x = 0.03 superconducting samples have been synthesized using conventional solid state reaction techniques. A Rietveld analysis of X-ray diffraction data for these specimens reveals that two structures (one tetragonal represented by T-YBCO, and the other orthorhombic represented by O-YBCO) co-exist at this composition of the cuprate. The use of a single tetragonal or single orthorhombic structure as the model for the refinements does not produce acceptable fits to the X-ray diffraction pattern. The refinements show that the T-YBCO phase at 298 K has tetragonal symmetry (*P4/mmm*) with $a = 0.387879(4)$ nm, $c = 1.17314(1)$ nm, and that the O-YBCO phase has at 298 K an orthorhombic symmetry (*Pmmm*) with $a = 0.387555(4)$ nm, $b = 0.389400(4)$ nm, $c = 1.17363(1)$ nm, respectively.

1. Introduction

The stoichiometry and oxygen ordering in the superconducting cuprates are crucial in determining the value of the critical temperature, T_c, which is depressed by an incorporation of substitutional ions. For $YBa_2Cu_3O_{7-\delta}$ (YBCO), this effect occurs for substitutions either in the Cu(1)–O chains or in the Cu(2)–O_2 sheets, suggesting that both of them play an important role in the superconductivity [1, 2]. To evaluate the relative importance of, the planar and square coordinated Cu(1) sites, cation doping has been widely applied to YBCO [3–7], because doping with Fe, Co, Ni, Au and Zn, onto the copper sites in YBCO, has significant effects on the superconducting properties. It is essential to determine the structure at a local level to fully understand the nature of superconductivity in these materials.

The effect of partial substitution of Co for Cu in YBCO on the superconducting critical temperature T_c has been extensively reported in the literature [8–13]. The Co dopant predominantly occupies the Cu(1) chain site over a wide range of Co concentrations. Evidence of the preferential substitution of Co for the Cu(1) chain site, accompanied with an increased oxygen content in the Cu(1)–O(1) planes has been provided by powder neutron diffraction [10] and Raman scattering [8] studies. In order to systematically study the structural variations in YBCO doped with small amounts of Co, single phase $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$($123Co_x$) samples were successfully synthesized. X-ray diffraction (XRD) studies [14] on these materials have revealed an abnormal behaviour in the structural parameters for the sample $123Co_{0.03}$.

In the present paper, the structure of a $123Co_{0.03}$ sample is carefully analysed using the Rietveld refinement technique. The structural parameters of a Co-rich tetragonal structured phase (T-YBCO) and an orthorhombic structured phase (O-YBCO) are obtained from the refinements.

2. Experimental procedure

The preparation procedures of the $123Co_x$ samples have been previously reported [14]. In this paper, only sample with the composition $123Co_{0.03}$ is studied. Measurement of the superconducting critical temperature was determined using standard four-probe techniques. The structure is characterized by the refinement of powder X-ray diffraction (XRD) data.

The $123Co_x$ powder was gently pressed into a standard Rigaku *Dmax* sample holder and was then carefully serrated with a razor blade to make a smooth surface and also to minimize any possible preferred orientation in the specimen.

The diffraction data for the Rietveld analysis was collected at room temperature (~298 K) with the Rigaku Dmax-rB powder diffractometer in the Bragg–Brentano geometry. The other parameters were diffracted-beam graphite (0002) monochromator, CuK_α radiation, a tube voltage of 40 kV and a tube current of 40 mA and a step scan-size of 0.02°, radius of the diffractometer 216 mm, with a counting time of 5 s per point, divergence slit DS = 1.0°, anti-scattering slit AS = 1.0°, receiving slit RS = 0.15 mm. The data was collected over the diffraction angle range of 20–90°. The collected powder diffraction pattern is shown in Fig. 1.

The Rietveld analysis was performed using the analysis program DBW3.2S [15]. The background was

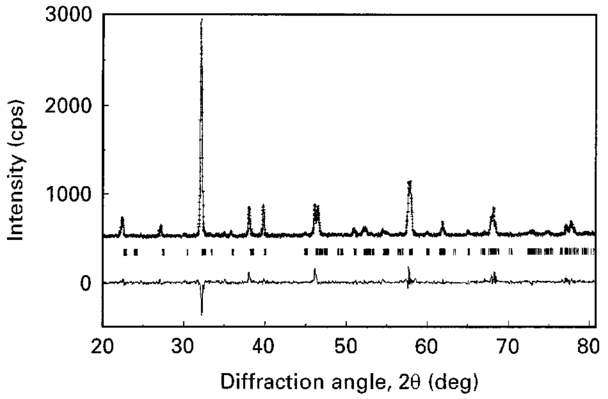

Figure 1 Rietveld refinement profiles for $123\mathrm{Co}_{0.03}$. (+) Are the X-ray diffraction data. The solid line is the calculated profile. A difference curve (observed results minus calculated ones) is plotted at the bottom.

refined using a fifth order polynomial. A pseudo-Voigt function was used to describe the peak shape. The Rietveld-Toraya model was applied to calculate the preferred orientation along (103). No absorption correction was applied to the raw data. The wavelengths of $\mathrm{Cu}K_{\alpha 1}$, $\mathrm{Cu}K_{\alpha 2}$ and the intensity ratio were 0.15406 nm, 0.15444 nm, and 0.497, respectively.

The refinement was performed by variation of the following parameters: (1) scale factor; background; zero point shift/sample displacement, transparency coefficient; (2) cell parameters; (3) peak shape; half width; asymmetry parameter and preferred orientation; (4) atom positions; (5) site occupancies; (6) overall thermal parameters; isotropic thermal parameters.

3. Results and discussion

Schmahl *et al.* [16] and Renevier *et al.* [17] have reported that the orthorhombic-to-tetragonal (O–T) phase transition for $123\mathrm{Co}_x$ samples occurred at a Co concentration of $x \sim 0.025$. The c lattice parameters were observed in both cases to increase with cobalt concentration. There are, to our knowledge, no reports about the co-existence of T-YBCO and O-YBCO phases. The diffraction data for $123\mathrm{Co}_{0.03}$ sample were first refined with either an orthorhombic symmetry or a tetragonal symmetry. However, these results were not completely satisfactory, and the refined parameters for single tetragonal or orthorhombic symmetry showed abnormal behaviour in comparison to other $123\mathrm{Co}_x$ ($0 \leqslant x \leqslant 0.08$, $x \neq 0.03$) samples [14]. No extra reflections are apparent in the diffraction pattern. However it is observed that the diffraction peaks are anomalously wide. In order to closely fit the measured XRD data, a combined T-YBCO and O-YBCO model was considered in our refinements.

The "R-factors" and the "goodness of fit" are used as numerical criteria for the level of the fit between the measured pattern and the calculated pattern. The definitions of the "R factors" and the "goodness of fit" are as follows:

pattern R-factor,

$$R_{\mathrm{p}} = \frac{\sum_{i=1}^{N} |Y_{\mathrm{oi}} - Y_{\mathrm{ci}}|}{\sum_{i=1}^{N} |Y_{\mathrm{oi}}|} \tag{1}$$

weighted pattern R-factor,

$$R_{\mathrm{wp}} = \left(\frac{\sum_{i=1}^{N} w_{\mathrm{i}}(|Y_{\mathrm{oi}} - Y_{\mathrm{ci}}|)^2}{\sum_{i=1}^{N} |Y_{\mathrm{oi}}|^2}\right)^{1/2} \tag{2}$$

expected R-factor,

$$R_{\mathrm{exp}} = \left(\frac{(N - P + C)}{\sum_{i=1}^{N} w_{\mathrm{i}} |Y_{\mathrm{oi}}|}\right)^{1/2} \tag{3}$$

and the "goodness of fit",

$$S = \frac{R_{\mathrm{wp}}}{R_{\mathrm{exp}}} \tag{4}$$

where, Y_{oi}, Y_{ci} are the observed and calculated intensities at the ith step, respectively, w_{i} is the weight ($=1/Y_{\mathrm{oi}}$), N is the total number of points, P is the number of parameters adjusted, and C the number of constraints applied.

Except for the sample with $x = 0.03$, the two phase refined R-factors for other samples are no better than

TABLE I Refined structural parameters of T-YBCO obtained by Rietveld analysis of X-ray powder diffraction data collected at 298 K with ESDs in parentheses. The structure has a symmetry of *P4/mmm* with $a = 0.387879(4)$ nm, $c = 1.17314(1)$ nm. Some selected interatomic distances (nm) are also listed

Atom	Site	x	y	z	B_{iso}	Occupancy
Y	1h	0.5	0.5	0.5	0.29(3)	1
Ba	2t	0.5	0.5	0.1845(5)	0.98(5)	1
Cu1	1a	0	0	0	1.67(4)	0.886(6)
Co1	1a	0	0	0	3.36(4)	0.114(6)
Cu2	2q	0	0	0.3596(7)	2.72(3)	1
O1	1e	0	0.5	0	1.66(23)	0.483(31)
O2	2q	0	0	0.1591(26)	1.72(34)	1
O3	4i	0.5	0	0.3837(41)	1.06(24)	1
Selected interatomic distances (nm)						
Y-03	0.237(2)	Ba-O3	0.304(2)	Cu2-O3	0.235(2)	
Ba-O1	0.2906(2)	Cu1-O1	0.193940(1)	Cu2-O2	0.196(3)	
Ba-O2	0.276(1)	Cu1-O2	0.187(2)	Cu1-Cu2	0.4219(2)	

TABLE II Refined structure parameters of O-YBCO obtained by Rietveld analysis of X-ray powder diffraction data collected at 298 K with ESDs in parentheses. The structure has a symmetry of *Pmmm* with $a = 0.387555(4)$ nm, $b = 0.389400(1)$ nm, $c = 1.17363(1)$ nm. Some selected interatomic distances (nm) are also listed

Atom	Site	x	y	z	B_{iso}	Occupancy
Y	1h	0.5	0.5	0.5	0.13(4)	1
Ba	2t	0.5	0.5	0.1859(5)	1.31(3)	1
Cu1	1a	0	0	0	1.86(7)	0.916
Co1	1a	0	0	0	4.29(4)	0.084(4)
Cu2	2q	0	0	0.3618(6)	1.87(5)	1
O1A	1a	0.5	0	0	1.36(15)	0.052(13)
O1B	1e	0	0.5	0	1.41(17)	0.884(21)
O2	2q	0	0	0.1669(14)	3.69(26)	1
O3A	2s	0.5	0	0.3741(28)	1.91(24)	1
O3B	2r	0	0.5	0.3941(32)	0.31(48)	1

Selected interatomic distances (nm)

Y–O3A	0.244(3)	Ba–O3A	0.294(2)	Cu2–O3A	0.194(4)
Y–O3B	0.230(3)	Ba–O3B	0.312(2)	Cu2–O3B	0.1984(7)
Ba–O1A	0.2924(2)	Cu1–O1A	0.193778(1)	Cu2–O2	0.229(2)
Ba–O1B	0.2918(2)	Cu1–O1B	0.194700(1)	Cu1–Cu2	0.4246(2)
Ba–O2	0.276(2)	Cu1–O2	0.196(2)		

those reported by Wu *et al.* [14]. However, the two phase refinements for the $123\mathrm{Co}_{0.03}$ sample are of high quality. The refined R-factors are as follows: the pattern R-factor $R_p = 7.894\%$, the weighted pattern R-factor $R_{wp} = 10.177\%$, and the expected R-factor $R_{exp} = 9.432\%$. The "goodness of fit" is $S = 1.079$. Tables I and II list the refined tetragonal and orthorhombic structural parameters. The estimated standard deviations (ESDs) are also included in the parentheses in Tables I and II. B_{iso} and x, y, z are the equivalent thermal parameter and the fractional coordinates, respectively. The data, fitting curves and the differences (residuals: $I_{obs} - I_{cal}$ where I_{obs} is the observed intensity and I_{cal} is the calculated intensity) are shown in Fig. 1. The structures of T-YBCO and O-YBCO are depicted in Fig. 2.

In the two coexisting structures model, the distribution of the Co on the Cu sites was tested in the following way. Initially, cobalt was placed exclusively on Cu(1), as has been found in previous studies of Co-doped samples [4, 7–14]. In later stages, a distribution on both positions was allowed, subject to the constraints that each site be fully occupied by the sum total of Co and Cu. These indicate that little, if any, cobalt substitutes in the "plane". The refined values for the Cu(2) site occupancy were $-1.37(4)$, and $-0.22(5)$ for the T-YBCO and O-YBCO, respectively. In the final models they were fixed at zero. The occupancy of the Cu(1) site was then allowed to vary freely, subject to the constraint that the site remained fully occupied. The refined numbers are in excellent agreement with the nominal stoichiometry, all falling within seven standard deviations of the ideal value (Tables I and II). These refinements indicate that the occupancy of Co in the Cu(2) site is negligible for both T-YBCO and O-YBCO phases. The validity of the model is further supported by the good fit to the data as shown in Fig. 1 which is reflected in the low value of S, which is 1.079. The result confirms and expands upon earlier extended X-ray absorption fine structure EXAFS and the neutron powder diffraction investigations of $123\mathrm{Co}_x$, where similar Co environments were observed [10, 12].

The oxygen atom occupancies were also investigated. However, the estimated standard deviations (ESDs) are relatively large due to the oxygen "insensitivity" to XRD. The refined results are also listed in Tables I and II. For the tetragonal structure there are three independent oxygen atoms (see Fig. 2). Two of them, O(2) and O(3), were found to be fully occupied

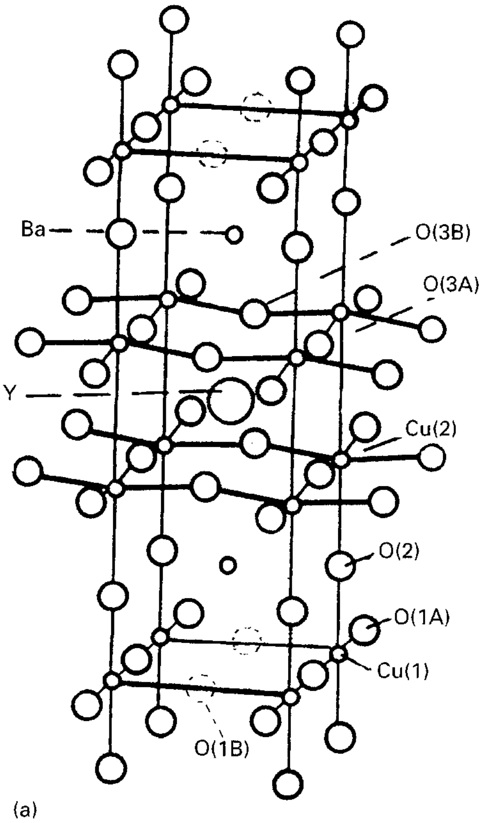

Figure 2 Continued

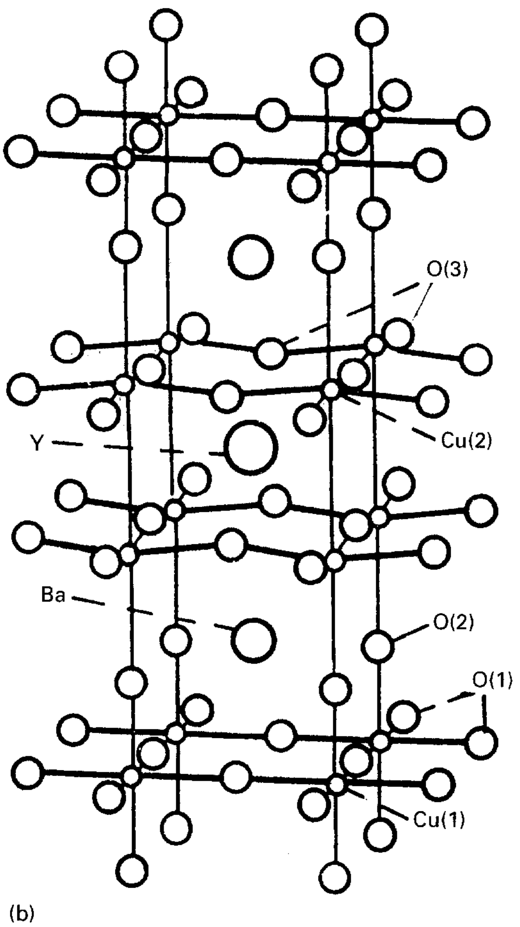

Figure 2 Structures of T-YBCO and O-YBCO phases. (a) Tetragonal structure, O(1) is not fully occupied by oxygen and Co partially occupies the Cu(1) site. (b) Orthorhombic structure, O(1A) and O(1B) are not fully occupied by oxygen, and the oxygen occupancy of site O(1A) is much larger than that in site O(1B). The cobalt partially occupies the Cu(1) site. The other sites are fully occupied by the corresponding atoms.

in the early refinements and fixed as such in subsequent work. The third atom, O(1), is in the plane of the "chain" metals and is known to be partially occupied in YBCO based materials. Due to the lower symmetry of the orthorhombic structure, there are five unique oxygen sites (Fig. 2). Three of these positions, O(2), O(3A) and O(3B) are related to those fully occupied in the tetragonal structure and are similarly fully occupied. The remaining two oxygen atoms, O(1A) and O(1B), correspond to O(1) in the tetragonal case, were found to be partially occupied. The slightly larger temperature factors for some atoms may result from a small local structure distortion.

The atomic coordinates, selected bond lengths for both T-YBCO and O-YBCO phases are calculated from the refinements and are listed in Tables I and II, respectively. The z fractional coordinate for Ba, Cu(2), O(2), O(3A) and O(3B) sites, varying with the Co content, are listed in Table III (for samples of $x \neq 0.03$ adopted from [14]). There is a dramatic variation in z values in the range of $0.02 \leqslant x \leqslant 0.04$. It is within this range that the O–T transition occurs.

The lattice constants of the T-YBCO and O-YBCO phases are both larger than those of 123Co_x ($0 \leqslant x \leqslant 0.08$, $x \neq 0.03$) samples. The reason for this abnormal behaviour is not yet fully understood. The oxygen content is, within the accuracy of our refinements almost the same. The refined Co concentration of the T-YBCO phase ($x = 0.038$) is larger than that of the O-YBCO phase ($x = 0.028$) and thus the T-YBCO phase can be considered to be a Co-rich phase. The reasons for the possible co-existence of T-YBCO and O-YBCO phases are as follows. The separation of the T-YBCO and O-YBCO phases may be due to a structural instability induced by the Co doping. The phase transition may occur at about $x = 0.03$, however the single tetragonal and orthorhombic $123\text{Co}_{0.03}$ phases are unstable. Thus a separation into a Co-riched tetragonal T-YBCO phase and a Co-poor orthorhombic O-YBCO phase occurs.

The ratio of crystalline T-YBCO and O-YBCO can be obtained by the following formula [18]:

$$W_{\mathrm{p}} = \frac{S_{\mathrm{p}}(M\Omega)_{\mathrm{p}}}{\sum_{\mathrm{i}}^{2} S_{\mathrm{i}}(M\Omega)_{\mathrm{i}}} \tag{5}$$

where we assume that the two phases being refined account for 100% of the specimen, i, p represents the tetragonal phase or orthorhombic phase, M is the atomic weight of the formula unit, Ω is the volume of the unit cell, S is the refined scale factor, which is obtained from:

$$Y_{\mathrm{ci}} = S_{\mathrm{j}} \sum_{\mathrm{k}} |F_{\mathrm{K}}|^2 \Phi(\Delta 2\theta) L_{\mathrm{K}} P_{\mathrm{K}} + Y_{\mathrm{bi}} \tag{6}$$

Y_{ci} and Y_{bi} are the calculated and background intensities, respectively; F_{K} is the structure factor; $\Phi(\Delta 2\theta)$ is the reflection profile function, i.e., in this case a pseudo-Voigt function: the Lorentz, polarization and multiplicity factors are contained in L_{K}; P_{K} is the Rietveld–Toraya preferred orientation function.

TABLE III Refined fractional co-ordinates of each atom along the z direction at room temperature for 123Co_x ($0 \leqslant x \leqslant 0.08$) samples. The atomic positions are: Y 1h($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), Ba 2t($\frac{1}{2}$, $\frac{1}{2}$, z), Cu(1) 1a(0, 0, 0), Cu(2) 2q(0, 0, z), O(1A) 1b($\frac{1}{2}$, 0, 0), O(1B) 1e(0, $\frac{1}{2}$, 0), O(2) 2q(0, 0, z), O(3A) 2s($\frac{1}{2}$, 0, z), O(3B) 2r(0, $\frac{1}{2}$, z). For $x \neq 0.03$, the total occupancy of oxygen sited at O(1A) nd O(1B) is fixed as 0.93, and the occupancy of the oxygen sited at O(1A) is fixed as 0.05 in the orthorhombic structure and as equal to O(1B) in the tetragonal one. The numbers in the parentheses are standard deviations of the last significant digit. Values for samples of $x \neq 0.03$ are adopted from [14].

z	0.0	0.01	0.02	0.03(O)	0.03(T)	0.04	0.06	0.08
Z_{Ba}	0.1841(5)	0.1856(5)	0.1863(9)	0.1859(5)	0.1845(5)	0.1837(5)	0.1851(4)	0.1866(4)
$Z_{\mathrm{Cu}}(2)$	0.3558(5)	0.3612(5)	0.3616(9)	0.3618(6)	0.3596(7)	0.3588(5)	0.3604(4)	0.3642(4)
$Z_{\mathrm{O}}(2)$	0.1672(5)	0.1668(5)	0.1661(9)	0.1669(14)	0.1591(26)	0.1626(5)	0.1607(4)	0.1587(4)
$Z_{\mathrm{O}}(3\mathrm{A})$	0.3795(5)	0.3885(5)	0.3907(9)	0.3741(28)	0.3837(41)	0.3878(5)	0.3704(4)	0.3697(4)
$Z_{\mathrm{O}}(3\mathrm{B})$	0.3645(5)	0.3802(5)	0.4074(9)	0.3941(32)	0.3837(41)	0.3878(5)	0.3704(4)	0.3697(4)

From the refinements, the overall scale factors are $(2.92 \pm 0.04) \times 10^{-7}$ and $(17.1 \pm 0.1) \times 10^{-7}$, respectively for the T-YBCO and O-YBCO phases. The relative concentrations of the phases are then calculated out to be 14.54 wt % (T-YBCO) and 85.46 wt % (O-YBCO).

4. Conclusions

The Rietveld analysis of powder diffraction data clearly demonstrates that the $123Co_{0.03}$ sample is composed of a two-phase mixture of T-YBCO (14.54 wt %) and O-YBCO (85.46 wt %). The Co content in T-YBCO is larger than that in the O-YBCO phase.

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