

# The Dependence of the Lattice Parameters on Oxygen Content in Orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ : A High Precision Reinvestigation of Near Equilibrium Samples

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A new high precision investigation of the unit cell geometry as a function of the oxygen content is presented for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . The differences from earlier work by other groups are (a) the use of “near-equilibrium,” i.e., not quenched but very slowly cooled samples; (b) the use of high accuracy volumetric oxygen determination; and (c) the large number of compositions investigated (36 in the range of  $0.5 < x < 1.0$ ). Special attention has been paid to very accurate control of the oxygen content during synthesis and to homogenization of the samples. A similarity to most of the work in the literature is that, differing from our previous work, the samples used here were synthesized from a carbonate Ba source. The results show that the parameters of the synthesis can influence the unit cell geometry. Thus, in samples synthesized with a Ba-carbonate precursor the *c*-parameter remains linear with the oxygen content. This is in agreement with the literature and opposite to our samples synthesized in the absence of carbonate. However, the *a*- and *b*-parameters change nonlinearly with the oxygen content, in agreement with our previous work with samples without carbonate precursors. For this reason the orthorhombicity shows a maximum corresponding to the  $T_c$  maximum. These deviations from linearity of the lattice parameters mirror lattice distortions and phase transitions in 123, briefly discussed here. Analytical functions are given which allow the estimation of the oxygen content from the lattice parameter.

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## INTRODUCTION

The superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (123) phase is one of the most investigated compounds in the last years. Due to its high transition temperature, stability to very large magnetic fields, and relatively easy synthesis, this material still attracts the attention of many research groups. An interesting and not completely clarified topic remains the influence of the structure (bond lengths, site occupation, substitution sites) and particularly its deformations on the superconduct-

tive properties. Recently, several theoretical models have stressed the importance of lattice distortions producing electronic inhomogeneities of various kinds (superstructures, phase separation, stripes, etc.) for understanding the mechanism of superconductivity (1–4). Although several indications of such phenomena have been discussed for the La cuprates (O- and Sr-doped) (4, 5) and the bismuthates (6), the evidence for the  $\text{YBaCuO}$  family has been rather ignored.

In the past we have performed investigations of the lattice constants in 123 as a function of the oxygen non-stoichiometry to find lattice distortions and phase transitions (7, 8) in samples synthesized either without carbonate or with drastic expulsion of it. Here, we extend this work to samples which, following the general trend of the literature, have been synthesized using Ba carbonate as starting material

The most important problem to solve in the course of such an investigation is the reproducibility of oxygen content distribution and determination. For this reason, in the past, several attempts, such as low temperature zirconium gettering (9), equilibration of samples with different oxygen contents (10), constant stoichiometry cooling (11) or quenching of samples (12, 27) have been made. The goal of the present work is to study “near-equilibrium” samples, that is, materials in which the defect structure is allowed to come as near as possible to equilibrium. To this end, the cooling rate was kept very low. Originally, the opinion prevailing in the literature was that at temperatures lower than  $500^\circ\text{C}$  the diffusion of oxygen is frozen. Oxygen diffusion measurements performed in our laboratory (13–15) have shown that this is not true and that diffusion is still appreciable even in the kinetically controlled regime at  $T < 250$  K.

The advantages of using powder samples for such investigations, as compared to single crystals, are the lower temperature of synthesis, the absence of flux (extraction of impurities from the walls), and the easy availability of larger samples. The first two lead to strong decrease in impurities

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(except carbonates) and the last allows high accuracy oxygen determination.

### EXPERIMENTAL

123 material of high oxygen content ( $x \leq 0.990$ ) was synthesized from high purity  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{BaCO}_3$  (99.99%), and  $\text{CuO}$  (99.99%) in six annealing steps for 35 h in oxygen, starting at  $860^\circ\text{C}$  and then increasing the temperature to  $935^\circ\text{C}$ . The low starting temperature prevents partial melting during the first synthesis steps caused by eutectics. The annealing at  $935^\circ\text{C}$  was repeated twice, for 75 and 50 h followed by cooling to room temperature at  $30^\circ/\text{h}$ . After each annealing step the samples were ground. The final step was annealing in oxygen at  $440^\circ\text{C}$  for 80 h and slow cooling to room temperature at a rate of  $10^\circ\text{C}/\text{h}$ .

To receive a given oxygen content, the samples were reduced by equilibration with yttrium turnings of exactly known weight in sealed silica ampules at  $600^\circ\text{C}$  for 15 h, with heating and cooling rates of  $10^\circ\text{C}/\text{h}$ . The 123 material and the yttrium turnings were placed in separate alumina crucibles inside the silica tube and then sealed. Thirty-six samples were prepared covering the oxygen homogeneity range of orthorhombic 123 ( $x = 0.45\text{--}0.990$ ). The volumetric method used for high accuracy determination of the oxygen content has been described elsewhere (16). Briefly, a sample is dissolved in dilute nitric acid and the volume of gaseous oxygen created by the reaction of the formal  $\text{Cu}^{3+}$  valence (more exactly  $[\text{Cu}\text{--O}]^{+p}$ ) with water is measured. Each sample was analyzed two times during this work using about 100 mg of powder. The reproducibility error of all the results was  $\pm 0.001$  in  $x$ . Samples of the composition  $x \cong 6.5$  cannot be analyzed by the volumetric method (no formal  $\text{Cu}^{3+}$  in the structure!). The iodometric titration normally used for determination of the oxygen content gives  $\pm 0.01$  precision in  $x$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , which is insufficient for high accuracy investigations. Thermobalance oxidations are often misleading because there is no definite reaction endpoint.

For the phase analysis X-ray powder diffraction was used. The detection limit of the method was estimated using calibration with known amounts of  $\text{BaCuO}_2$ , the most common impurity in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . Careful measurements with different well-known amounts of  $\text{BaCuO}_2$  between 1 and 10 wt.% made it possible to deduce by extrapolation a detection limit of 0.5 wt.%. The impurity content of the investigated samples was well below this limit.

For the lattice parameter determination, the samples were measured on a STOE powder diffractometer, using silicon ( $a = 5.43088 \text{ \AA}$ ) as an internal standard. Data were recorded in transmission geometry in the  $2\theta$  range between  $5^\circ$  and  $120^\circ$  using Ge-monochromatized  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ). More than 30 reflections were used to determine the parameters in the orthorhombic space group

*Pmmm*. Selected samples were again measured with same geometry without silicon for Rietveld refinements.

Because of the low scattering power of oxygen for X-rays a refinement of the oxygen site occupations was not performed. Therefore, the oxygen occupancies were fixed to 100% during the Rietveld refinements, except the O(4) position. This was assumed to correspond to the value obtained from the oxygen content determination. A possible occupation of the O(5) position had to be neglected. The metal occupancies were fixed to 100%, with the exception of the occupation of the Cu(1) position (chain copper).

The refinements converged at rather low disagreement factors between observed and measured intensities with final  $0.04 < R_1 < 0.08$  and  $0.05 < R_{\text{wp}} < 0.08$ .

In view of the two different nomenclatures for the oxygens of the 123 structure, we note that O(4) is used for the oxygen of the chains along the *b*-axis and O(5) for the bridging sites between the Cu1 of two adjacent chains.

### RESULTS AND DISCUSSION

A comparative discussion of the lattice parameters and some physical properties as a function of doping of 123 samples synthesized with various methods and showing the existence of a displacive structural phase transition at  $x = 0.95$  is given elsewhere (17).

We note that samples synthesized under the above conditions using Ba carbonate as a starting material are very homogeneous. This is clearly shown, from the high reproducibility of the lattice parameters of different batches (Figs. 1 and 2). The higher homogeneity could be due to traces of carbonate, located in the grain boundaries, functioning as a flux and, therefore, increasing the velocity of the reaction by decreasing the activation energy. However, this does not mean necessarily that all the structural properties of these samples can be considered as intrinsic (17). The fact that in these samples only traces of carbonate exist has been shown in the past by mass spectrometry combined with thermogravimetry (18).

The main difference in the lattice parameters of these samples from those described in the literature is their nonlinear dependence on the oxygen doping. Figure 1 shows these results. The *c*-axis has linear behavior, whereas the *a*-axis is a smooth parabola and *b* clearly shows a maximum at about 6.85 as a function of the oxygen content. The smallest effects are observed in the *b*-axis where the whole variation is in the range of  $0.01 \text{ \AA}$  ( $0.02 \text{ \AA}$  in the *a*- and  $0.06$  in the *c*-axis).

The nonlinearity of the lattice parameters has been observed first by X-ray diffraction particularly for the *c*-axis (22), in samples synthesized without using carbonate. Later this was confirmed with neutron diffraction (in the same samples) and showed that the minimum of the *c*-axis was associated to a structural transition in the buckling

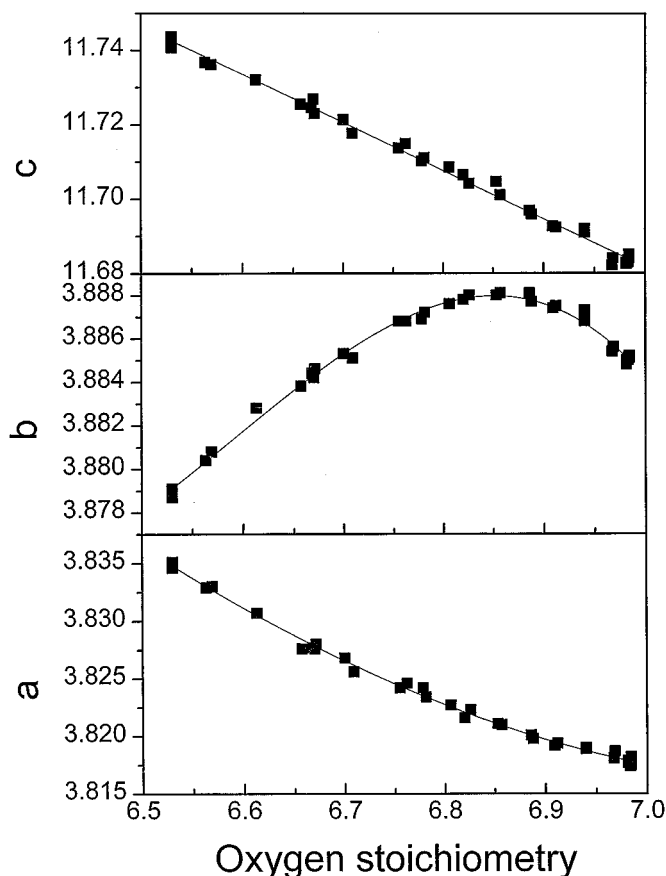


FIG. 1. Lattice parameters  $a$ ,  $b$ ,  $c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  as a function of oxygen stoichiometry. Standard deviations are smaller than the size of the symbols. The lines show the analytical fits. Note that samples of different batches fall exactly in the same fits.

(contraction of the  $\text{Cu}_2\text{-O}_{2/3}$  bond) of the superconducting planes, taking place at the onset of the overdoped region  $x \cong 6.92$  (8). The present results show for the first time that this structural anomaly is masked when Ba carbonate is used as starting material and therefore explains why other laboratories using Ba carbonate could not observe this effect. It is very interesting that in spite of the linear behavior of the  $c$ -axis, our Ba-carbonate samples do show this structural transition with Raman scattering (strong softening of the  $\text{Cu}_2\text{-O}_{2/3}$  mode at  $x \cong 0.95$ ) (23). Also, recent EXAFS measurements of the same 123 samples, the first performed as a function of stoichiometry and temperature, show that in this range a change of the mechanism of  $\text{Cu}_2\text{-O}_{2/3}$  contraction takes place with increasing oxygen doping, associated for  $x > 0.9$  with a distortion of the  $\text{CuO}_5$  pyramids (24).

Both the samples synthesized with Ba carbonate and those synthesized with oxidized Ba-metal (8) do show, however, when they are not quenched but slowly cooled to room temperature, a nonlinear dependence of the  $a$ - and  $b$ -axes on oxygen doping. An explanation for that is probably the

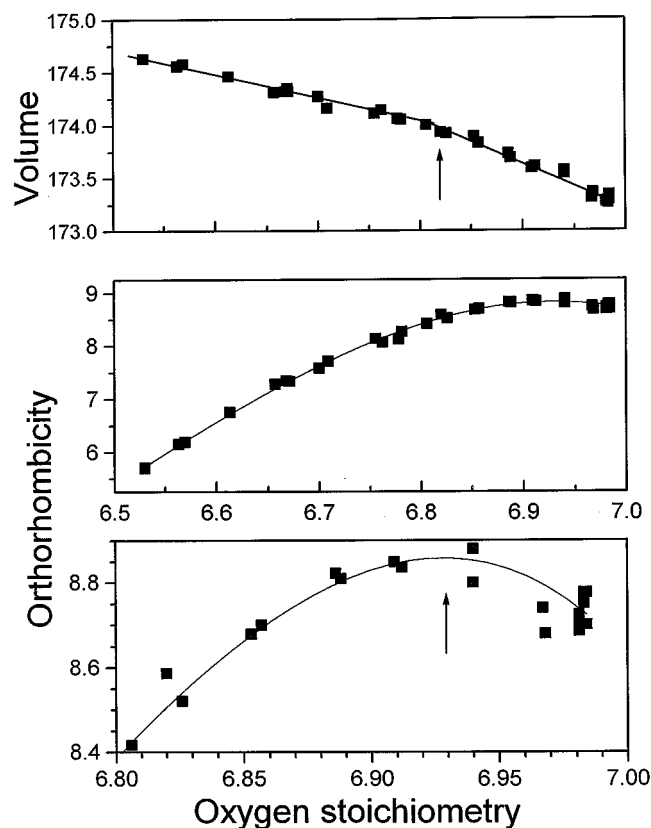


FIG. 2. Cell volume and orthorhombicity  $1000(b - a)/(b + a)$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  as a function of oxygen stoichiometry. Lower figure in higher magnification to show the existence of a maximum in the orthorhombicity.

occupation of the O5 site under near-equilibrium conditions. With increasing oxygen content we would then expect relative expansion of the  $a$ -axis and contraction of the  $b$ -axis. This is exactly what the experiment shows. At approximately  $x = 0.65$  the  $a$ -axis starts decreasing more slowly and the  $b$ -axis starts increasing slower with oxygen doping (Fig. 1). In samples synthesized by a similar method as in this work, structure refinement by neutron powder diffraction showed a 4% occupancy (with a standard deviation of 1%) of the O5 site for  $x = 0.996$  (25). Also in R-123 samples differently synthesized but still not quenched a similar O5 occupation has been found (26). We note that O(4) sites in twin domains smaller than approx.  $1000 \text{ \AA}$  may appear as O(5) atoms of the average structure if powder methods are used for the determination. The high reproducibility of both oxygen content and lattice parameter values and the large number of stoichiometries investigated in this work allows to prove clearly the existence of a flat maximum in the  $b$ -axis at approx.  $6.83 < 6 + x < 6.92$  (Fig. 1), where previous investigations (see, e.g., Refs. 9, 19) showed saturation behavior. The clear decrease of the  $b$ -axis in the overdoped range indicates that the interaction leading to

O-vacancies in the chains becomes much stronger at very high oxygen concentrations. Near-equilibrium samples, therefore, should be expected to have oxygen vacancies in the O4 sites of the chains, even at very high oxygen concentrations. It seems reasonable to assume that the oxygen content compensation derives from the occupation of the O5 sites ( $a$ -axis relative increase).

An additional effect influencing the decrease of the  $b$  parameter for  $x > 6.85$  is possibly due to the introduction of defects at the Cu(1) site, preventing the formation of longer chains. The Rietveld refinement showed a decreased occupancy of the Cu(1) sites. The refined Cu(1) occupancy is independent of the oxygen content and varies between 0.88 and 0.93. This is due to the incorporation of defects at the Cu(1) site. These defects are carbonate or Al vacancies or any other impurities. The same effects were observed and discussed in detail for single crystal (28) and powder refinements (15) of YBCO-247. We note here that the 90% occupancy of the Cu1 site does not mean the incorporation of a stoichiometric amount of carbonate. We have found with mass spectrometry combined with thermogravimetry (18) that the carbonate content of these samples is of the order of 1000 ppm.

The Cu(1) deficiency also opens the question of the maximum oxygen content of these samples. It is possible that the theoretical value of the highest stoichiometry ( $6 + x = 7$ ) is not reached, but instead the maximum value in our samples stays at 6.990, due to the impurities and vacancies associated with the Cu(1) deficiency.

The maximum in the  $b$ -axis and the parabolic form of the  $a$ -axis induce a maximum in the orthorhombicity  $or = 1000(b - a)/(b + a)$  and a change of slope in the cell volume dependence on doping (Fig. 2). The orthorhombicity is, therefore, mimicking the dependence of the  $T_c$  on doping (8, 20, 21, 27).

All the above deviations for linearity indicate increased interactions taking place in the overdoped range.

The high reproducibility of the lattice parameters as a function of the oxygen content found in this work triggers the temptation to give mathematical fits of these curves in order to obtain reference data. The advantage would be oxygen content estimation requiring only a very small amount of a sample, which could be important, e.g., in the case of single crystal investigations (provided that the different chemistry of synthesis does not interfere). It should also be possible to use the absolute lattice parameter values as a reference; they are related to the internal Si standard. On the other hand, possible lack of reproducibility of these data for samples from other laboratories could lead to misunderstandings.

The fits of the lattice parameters  $a, b, c$  as functions of the oxygen content are shown in Fig. 1 as thin solid lines. Equations [1]–[3] enable the lattice parameters to be calculated as a function of  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . With

Eqs. [4]–[9] it is possible to estimate the oxygen content of 123 samples from the lattice parameters and the orthorhombic distortion  $or = 1000(b - a)/(b + a)$ :

$$a = 3.87498 - 0.09655x + 0.03908x^2 \text{ [\AA]} \quad [1]$$

$$b = 3.89605 - 0.15166x + 0.323x^2 - 0.18324x^3 \text{ [\AA]} \quad [2]$$

$$c = 11.8114 - 0.1298x \text{ [\AA]} \quad [3]$$

For Eqs. [4]–[9] the following substitutions are made:

$$a' = a - 3.81; \quad b' = b - 3.87; \quad c' = c - 11.6.$$

$$x = 1.32614 - 50.46a' + 750.28a'^2 \quad [4]$$

$$x = 0.60591 - 28.357b' + 2276.7b'^2 \quad \text{for } x < 0.85 \quad [5]$$

$$x = -1.82154 + 372.28b' - 12365b'^2 \quad \text{for } x > 0.85 \quad [6]$$

$$x = 1.6231 - 7.6524c' \quad [7]$$

$$x = -2.49528 + 1.26105or - 0.18078or^2 + 0.0092203or^3 \quad \text{for } x < 0.92 \quad [8]$$

$$x = -125.19611 + 29.08491or - 1.670676or^2 \quad \text{for } x > 0.92. \quad [9]$$

For a quick estimate of the oxygen concentration it is sufficient to use the  $c$ -parameter and Eq. [7]. More reliable results are obtained by averaging the results of Eqs. [5]–[9]. The error of such a determination should be smaller than 0.01 in  $x$ , provided that the samples used here can be reproduced elsewhere. Table 1 compares experimental results with calculated data from Eqs. [1]–[9].

Figure 3 shows the  $z$ -coordinates of the atoms ( $z$ - for Cu(1) = 0 Å) resulting from the Rietveld refinements. As expected (see, e.g., Refs. 9, 18), with increasing oxygen content a reduction of the apical bondlength Cu(2)–O(1) and an elongation of the Cu(1)–O(1) bond is observed. Ba moves toward the CuO chains, attracted by the increased negative charge at the basal plane. The remaining atoms follow this trend, leading to a decrease of the  $c$ -axis with increasing oxygen concentration. An exception is the O(2) and O(3) atoms of the CuO<sub>2</sub> planes, which are shifted toward Y at  $x > 0.8$ , as explained elsewhere (8, 17). This increases the buckling of the CuO<sub>2</sub> plane (the spacing between Cu(2) and the averaged O(2, 3) plane) (Fig. 4) and decreases the distance between the oxygen planes adjacent to the yttrium atom layer. In spite of the lower sensitivity of the X-rays for O, this reflects to some degree the findings of the neutron diffraction in samples synthesized without carbonate (8, 17). Although the phase transition at  $x > 0.92$  found by neutron

**TABLE 1**  
**Comparison of Experimental and Calculated Values for Lattice Parameters and Oxygen Content**

Oxygen content (experimental)	Oxygen content (calculated)	$a$ [Å]	$b$ [Å]	$c$ [Å]
6.983(2)	6.982	3.8174(2) <i>3.8178</i>	3.8850(1) <i>3.8850</i>	11.6829(5) <i>11.6838</i>
6.983(2)	6.980	3.8177(2) <i>3.8178</i>	3.8851(1) <i>3.8850</i>	11.6835(5) <i>11.6842</i>
6.888(1)	6.894	3.8198(2) <i>3.8201</i>	3.8877(2) <i>3.8878</i>	11.6958(7) <i>11.6961</i>
6.886(2)	6.883	3.8201(2) <i>3.8201</i>	3.8881(2) <i>3.8878</i>	11.6968(7) <i>11.6964</i>
6.657(2)	6.661	3.8276(2) <i>3.8284</i>	3.8838(2) <i>3.8839</i>	11.7254(9) <i>11.7261</i>
6.668(2)	6.669	3.8277(2) <i>3.8279</i>	3.8844(2) <i>3.8842</i>	11.7245(8) <i>11.7247</i>

*Note.* Lattice parameters in italics are calculated from experimental oxygen contents using Eqs. [1–3]; oxygen contents are calculated from observed lattice parameters using the averages of Eqs. [4–9].

diffraction (8) and supported by EXAFS (17, 24) cannot be resolved, the increased buckling is clearly seen.

### CONCLUSIONS

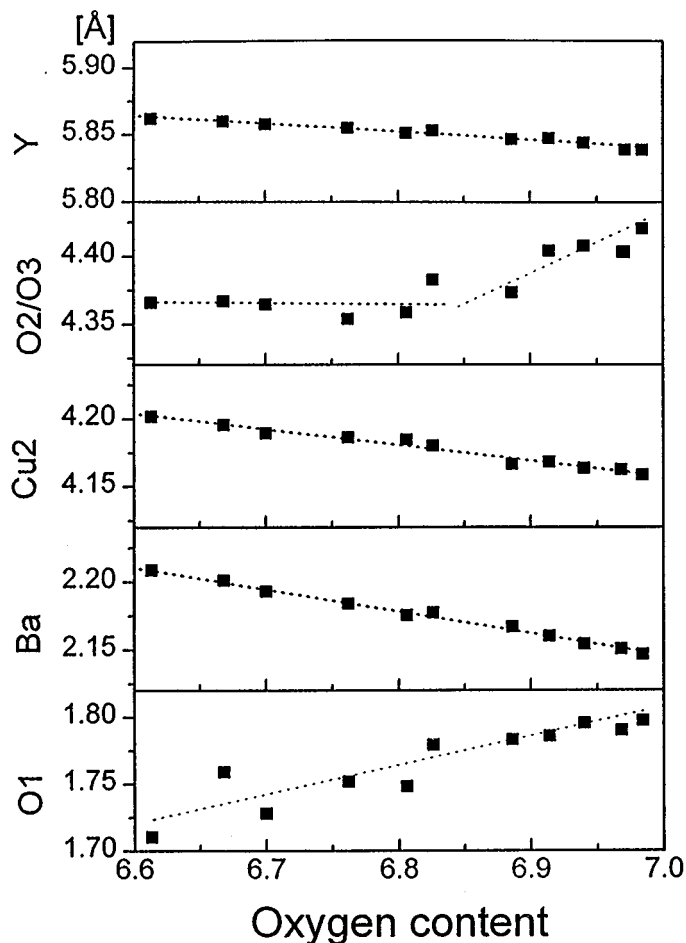
An investigation of the structure of slowly cooled (near-equilibrium) 123 samples synthesized with Ba carbonate as a function of the oxygen content has been performed. Particular attention has been given to the changes of the lattice parameters. The samples have been characterized with high accuracy volumetric oxygen analysis, with dc magnetization (21), and with Raman (23) and EXAFS (24) measurements. A review of the results is given elsewhere (17).

The main results of the present structural study are:

(1) The nonlinearity of the  $a$  and  $b$  lattice parameters, which leads (a) to a maximum of the orthorhombicity at the onset of the overdoped range, mimicking the  $T_c$  dependence on oxygen doping, and (b) an additional contraction of the cell volume at the onset of the overdoped range.

(2) The high reproducibility and homogeneous distribution of defects, possibly due to the flux function of carbonate traces. Analytical fits can therefore be given for the lattice parameters and the orthorhombicity as functions of the oxygen content.

(3) The lack of minimum of the  $c$ -parameter at the onset of the overdoped range in contrast to our samples synthesized without Ba carbonate (by direct oxidation of Ba metal). However, the present samples do show at the same composition ( $x = 0.95$ ) anomalies of the Raman scattering (O2–O3 in-phase vibrations) due to the structural transition (17). EXAFS measurements in the same samples confirm



**FIG. 3.** Atom positions [Å] as a function of the oxygen stoichiometry of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  as determined by Rietveld refinements of powder diffraction data. The distance corresponds to the height above the basal ( $z = 0$ ) plane, containing Cu(1)–O chains.

this structural anomaly and indicate a complex structural transition in the distortion of the  $\text{CuO}_5$  pyramids (24).

We conclude, therefore, that interesting lattice distortions do take place as a function of the oxygen doping in 123, particularly in the overdoped range. Unfortunately, more information cannot be extracted from powder measurements. For fine details, e.g., if the buckling anomalies are related to stripe formation in the superconducting planes, single crystals of very good quality without aluminium doping and with nearly theoretical occupancy of Cu1 are necessary. When such crystals are available, the problem of the exact oxygen determination remains. The highly accurate volumetric method we use is destructive and needs approx. 100 mg of substance. An indirect method of oxygen determination could be via the lattice constants, as shown above, or for more sophisticated determination, the Raman phonons as a function of the oxygen stoichiometry (see, e.g., 23).

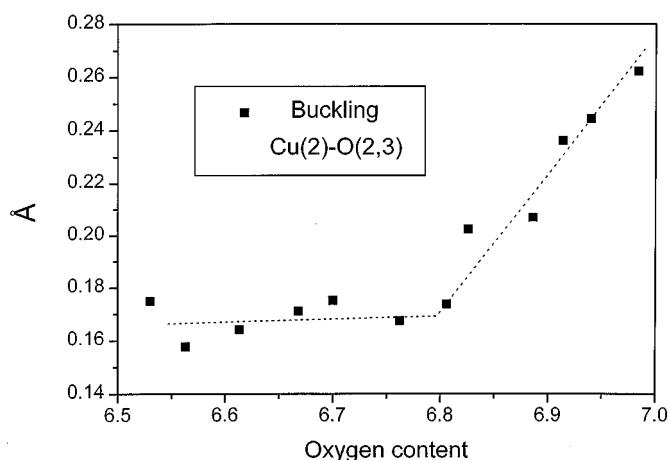


FIG. 4. Buckling of the  $\text{CuO}_2$  plane as a function of oxygen content. For a discussion see the text.

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