Superconducting Cuprates and Related Oxides, V. Composition and Structure of Single Crystals Grown on an Alumina Matrix: $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31(2)}$ and $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$

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The composition of the tetragonal cuprates $REBa_2Cu_3O_{7-\delta}$ (RE = Y and Ho) was investigated by X-ray and neutron single crystal diffraction analysis and by electron microprobe analysis. The combination of the neutron diffraction analysis and the electron microprobe analysis on the same crystal samples yielded the compositions $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31(2)}$ and $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$, respectively. The single crystals were grown in an Al_2O_3 crucible from a BaO–CuO flux, and the Al content in the crystals comes from the crucibles used.

The ternary cuprate $YBa_2Cu_3O_{7-\delta}$ exists in two crystallographic modifications depending upon the oxygen content. The orthorhombic form with δ close to zero is the high-T_c material with transition to superconductivity in the 80–90 K temperature range. The tetragonal modification with δ close to one shows no high-T_c superconductivity. Single crystals of the tetragonal form of $YBa_2Cu_3O_{7-\delta}$ can be grown from a high-temperature solution containing BaO and CuO.[1-3] The present crystallographic investigation of the tetragonal forms of the yttrium and holmium cuprates shows, in addition to the oxygen nonstoichiometry, a solid solution with aluminium from the crucible used in the crystal growth, so that the compositions are $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31(2)}$ and $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$, respectively.

A number of crystal structure investigations have been reported for the tetragonal $REBa_2Cu_3O_{7-\delta}$ (RE = Y and lanthanide elements). In these works it is often observed that the copper atom Cu1 in site 1a has a relatively high value of the thermal parameter. This could be due to a copper nonstoichiometry, vacancies in site 1a, or to a solid solution of copper with a metal with a lower scattering capacity. Such a copper–metal solid miscibility is more likely to occur in crystals grown from a high-temperature flux than in polycrystalline samples made in solid-state sintering reactions. In the former case the flux may corrode the crucible and thus provide metal ions for a copper–metal solid solution in the crystals; in the latter case the contact between the solid reaction mixture and the crucible is limited, and contamination of the sample with metal ions from the crucible material is less likely than in the former

case. A high thermal parameter of Cu1 observed for structures derived from samples made in solid-state sintering reactions may thus be interpreted as a combination of copper atoms and vacancies in site 1a rather than a copper–metal-atom solid solution in the site. An X-ray powder diffraction analysis of the structure of $YBa_2Cu_3O_7$ and a single-crystal X-ray analysis of the same structure did not include investigation of a copper deficiency.[4,5] An X-ray single-crystal analysis of the structure of $YBa_2Cu_3O_7$ and an X-ray powder diffraction least-squares profile refinement of the structure of $LaBa_2Cu_3O_7$ included investigations of the Cu1 nonstoichiometry and that of O1.[6-8] A neutron powder diffraction least-squares profile refinement of the structure of $YBa_2Cu_3O_7$ deals with the O1 nonstoichiometry.[9] Recent work on $YBa_2Cu_3O_{7-\delta}$ describes electron density distributions obtained from powder X-ray diffraction data,[10] single-crystal X-ray analyses of $YBa_2Cu_3O_{7-\delta}$ and $HoBa_2Cu_3O_{7-\delta}$,[11] determinations of electron densities and atomic charges in $YBa_2Cu_{2.93}O_{6.38}$ from X-ray analysis,[12] and the oxygen order in $YBa_2Cu_3O_{6.3}$ studied by single-crystal neutron diffraction analysis.[13] All these studies (Refs. 10–13) deal with the oxygen nonstoichiometry, but only in Ref. 12 is the copper deficiency taken into consideration as well as the oxygen nonstoichiometry.

Experimental and results

The single crystals of $YBa_2Cu_{3-\epsilon}Al_yO_{7-\delta}$ and $HoBa_2Cu_{3-\epsilon}Al_yO_{7-\delta}$ were grown from a BaO–CuO flux as described previously.[14]

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Table 1. Refined parameters from the single-crystal X-ray diffraction analysis of $YBa_2Cu_3O_{7-\delta}$.[a]

Atom	Site	Occupancy	x/a	y/b	z/c	B/Å²
Y	1d	1.0	1/2	1/2	1/2	0.83(2) 0.44(2)
Ba	2h	2.0	1/2	1/2	0.1922(1) 0.1922(1)	0.91(1) 0.88(2)
Cu1	1a	0.89(1) 0.87(1)	0	0	0	1.18(4) 1.13(5)
Cu2	2g	2.0	0	0	0.3606(1) 0.3609(2)	0.43(2) 0.33(2)
O1	2g	1.87(10) 1.77(10)	0	0	0.1519(13) 0.1534(17)	2.02(20) 1.75(23)
O2	4i	4.0	0	1/2	0.3785(5) 0.3770(6)	0.57(6) 0.26(8)
O3	2f	0.18(8) 0.27(11)	0	1/2	0	2.00 2.00

[a]Space group P4/mmm (No. 123). For each atom are listed coordinates from $MoK\alpha$ data (first line) and from $AgK\alpha$ data (second line). Isotropic extinction parameter. 0.000 46(2) ($MoK\alpha$ data); 0.000 25(2) ($AgK\alpha$ data).

Single-crystal X-ray diffraction analysis of $YBa_2Cu_{3-x}Al_y$-$O_{7-\delta}$. The single crystal used in the diffraction measurements had the dimensions $0.250 \times 0.125 \times 0.138$ mm³. The X-ray diffraction data were measured on a Huber four-circle diffractometer using $Mo\,K\alpha$ radiation (λ = 0.7107 Å). Diffraction data from 25 reflections were used to calculate the unit cell parameters in a least-squares refinement yielding the values $a = 3.873(4)$ and $c = 11.704$ (15) Å. The reflections in a sphere with the limits of the Miller indices $-6 \le h \le 6$, $-6 \le k \le 6$, $-21 \le l \le 21$ were measured, giving a total of 3760 reflections including two standard reflections for every 50 reflections. An absorption correction was applied to the data, $\mu_{Mo} = 290$ cm⁻¹, by Gaussian integration. The transmission range of the absorption corrections was 0.04–0.16. After averaging the symmetry-related reflections, 737 reflections with $I > \sigma(I)$

were obtained. The R-values on averaging the reflections were $R = 5.9\%$ and $R_w = 5.9\%$, where $R = 100 \times \Sigma |F - F_{av}| / \Sigma F$ and $R_w = 100 \times \Sigma |F_w - F_{wav}| / \Sigma F_w$.

Another set of data was measured with the same crystal using $Ag\,K\alpha$ radiation ($\lambda = 0.5608$ Å), with 4671 reflections, some of which were measured twice. The reflections in the sphere were restricted by the Miller indices limits $-6 \le h \le 6$, $-6 \le k \le 6$, $-20 \le l \le 20$. An absorption correction was made with $\mu_{Ag} = 154$ cm⁻¹. In this case the transmission range of the absorption was 0.15–0.29. Using the same procedure as above, 529 independent reflections with $I > \sigma(I)$ were obtained. The R-values on averaging were $R = 11.0\%$ and $R_w = 11.2\%$.

The model of the structure from Ref. 9 was refined by a least-squares procedure using the program LINUS.[15] Form factors for neutral atoms were applied.[16] The refinement gave a final R-value of 5.6% for each of the two sets of data. Table 1 displays the final values of the refined parameters. Except for the isotropic temperature factor parameters, the results from the two sets of data do not deviate significantly from each other.

Single-crystal neutron diffraction analysis of $HoBa_2Cu_{3-x}$-$Al_yO_{7-\delta}$. The single crystal used in the diffraction measurements had the dimensions $1.4 \times 2.4 \times 2.6$ mm³. The data were measured on a Huber four-circle diffractometer at DR3, Risø, using a neutron wavelength $\lambda = 1.0120$ Å. The reflections in a sphere with the Miller indices limits $-5 \le h \le 5$, $-5 \le k \le 5$, $-17 \le l \le 17$ were measured. This gave 2392 reflections, including three standard reflections for every 50 reflections. An absorption correction was applied to the data by Gaussian integration with $\mu = 0.284$ cm⁻¹. The transmission range was 0.94–0.96. After taking averages of the symmetry-related reflections, the number of independent reflections with $I > \sigma(I)$ was 386. The R-values on averaging were $R = 2.3\%$ and $R_w = 3.0\%$.

The model of the structure was refined using the least-squares program LINUS,[15] the model was that taken from

Table 2. Refined parameters from the single-crystal neutron diffraction analysis of $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$.[a]

Atom	Site	Aluminium contribution not included $R = 2.9\%$, $R_w = 2.1\%$				Aluminium contribution included $R = 2.9\%$, $R_w = 2.1\%$				$U_{11} = U_{22}$	U_{33}
		A^b	x/a	y/b	z/c	A^b	x/a	y/b	z/c		
Ho	1d	1.0	1/2	1/2	1/2	1.0	1/2	1/2	1/2	0.0061(3)	0.0082(5)
Ba	2h	2.0	1/2	1/2	0.190 61(12)	2.0	1/2	1/2	0.190 62(12)	0.0119(3)	0.0115(5)
Cu1	1a	0.939(8)	0	0	0	0.890(8)	0	0	0	0.0140(5)	0.0090(7)
Al	1a	0.0	0	0	0	0.11(1)	0	0	0	0.0140(5)	0.0090(7)
Cu2	2g	2.0	0	0	0.359 13(8)	2.0	0	0	0.359 12(8)	0.0055(2)	0.0114(4)
O1	2g	1.950(14)	0	0	0.154 79(12)	1.950(14)	0	0	0.154 80(12)	0.0210(5)	0.0155(7)
O2	4i	4.0	0	1/2	0.378 19(7)	4.0	0	1/2	0.378 19(7)	0.0073(2)	0.0123(4)
O3	2f	0.585(16)	0	1/2	0	0.585(16)	0	1/2	0	0.0273(20)	0.0220(28)
		Isotropic extinction parameter: 0.000 156(10)				Isotropic extinction parameter: 0.000 156(10)					

[a]Space group P4/mmm (No. 123). Unit cell parameters $a = 3.8587(3)$, $c = 11.719(1)$ Å. $^b A$ is the Wyckoff number times occupancy.

Table 3. Refined parameters from the single-crystal neutron diffraction analysis of $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31(2)}$.[a]

Atom	Site	Aluminium contribution not included $R = 3.0\%$, $R_w = 2.3\%$				Aluminium contribution included $R = 3.0\%$, $R_w = 2.3\%$				$U_{11} = U_{22}$	U_{33}
		A^b	x/a	y/b	z/c	A^b	x/a	y/b	z/c		
Y	1d	1.0	1/2	1/2	1/2	1.0	1/2	1/2	1/2	0.0066(3)	0.0127(6)
Ba	2h	2.0	1/2	1/2	0.192 74(13)	2.0	1/2	1/2	0.192 74(13)	0.0118(4)	0.0148(7)
Cu1	1a	0.918(8)	0	0	0	0.874(8)	0	0	0	0.0158(6)	0.0117(8)
Al	1a	0.0	0	0	0	0.10(1)	0	0	0	0.0158(6)	0.0117(8)
Cu2	2g	2.0	0	0	0.359 97(9)	2.0	0	0	0.359 97(9)	0.0055(2)	0.0148(4)
O1	2g	1.894(15)	0	0	0.153 70(15)	1.894(15)	0	0	0.153 70(15)	0.0215(5)	0.0176(8)
O2	4i	4.0	0	1/2	0.378 58(8)	4.0	0	1/2	0.378 58(8)	0.0073(2)	0.0163(4)
O3	2f	0.413(16)	0	1/2	0	0.413(16)	0	1/2	0	0.0295(31)	0.0232(43)
		Isotropic extinction parameter: 0.000 125(10)				Isotropic extinction parameter: 0.000 125(10)					

[a]Space group $P4/mmm$ (No. 123). Unit cell parameters $a = 3.8614(3)$, $c = 11.736(1)$ Å. [b]A is the Wyckoff number times occupancy.

the X-ray single-crystal analysis and the atomic scattering lengths were from Ref. 17. The final R-value was 2.9%, and the values of the refined parameters are listed in Table 2.

Single-crystal neutron diffraction analysis of $YBa_2Cu_{3-\varepsilon}-Al_yO_{7-\delta}$. The single crystal used had the dimensions $1.0 \times 3.8 \times 4.0$ mm³, and the data were measured on the same diffractometer as above. The reflections in the sphere with Miller-index limits $-5 \leq h \leq 5$, $-5 \leq k \leq 5$, $-17 \leq l \leq 17$ gave 2527 reflections, including three standard reflections for every 50 reflections. Absorption corrections made as above with $\mu = 0.050$ cm^{-1} showed a transmission range of 0.983–0.995. The average of symmetry-related reflections gave 386 reflections with $I > \sigma(I)$, and the R-values on averaging were $R = 4.6\%$ and $R_w = 4.8\%$. Model calculations as above gave a final R-value of 3.0%. The values of the refined parameters are listed in Table 3.

Microprobe analysis of the two crystals used in the neutron diffraction measurements. The crystals of $YBa_2Cu_{3-\varepsilon}Al_y-O_{7-\delta}$ and $HoBa_2Cu_{3-\varepsilon}Al_yO_{7-\delta}$ used in the single-crystal neutron diffraction measurements were mounted in an epoxy resin so that a crystal edge could be polished and examined in an electron microprobe. The instrument used was a JEOL JXA-8600 superprobe, using the Tracor software TASK for instrument control and PRZ (atomic number, absorption and fluorescence) corrections. The instrument operates with a potential of 20 kV and a beam current of 10 nA, and has a focal spot of ca. 2 μm. The wavelength analysis of the X-rays emitted from the sample is made with flow proportional counters using 90% Ar and 10% CH₄ and sealed Xe proportional counters. The following spectral lines and standards were used in the analysis: $Ho\,L\alpha$: a synthetic glass standard REE4 containing 4.41% Ho_2O_3;[18] $Ba\,L\alpha$: baryte, $BaSO_4$; $Cu\,K\alpha$: Cu; $Y\,L\alpha$: a stoichiometric alloy of YCu; $Al\,K\alpha$: synthetic Al_2O_3. The analytical conditions for the different lines are listed in Table 4. The $Al\,K\alpha$ line is close to the third-order $Ba\,L\alpha$ line, but this inter-

Table 4. Analytical conditions for the microprobe analysis.

X-Ray line	Analyser crystal[a]	X-Ray detector
$Ho\,L\alpha$	LiF (200)	XePC
$Cu\,K\alpha$	LiF (200)	XePC
$Ba\,L\alpha$	PET	XePC
$Y\,L\alpha$	PET	XePC
$Al\,K\alpha$	TAP	GFPC

[a]PET, pentaerythritol (002); TAP, thallium acid phthalate (100); XePC, xenon proportional counter; GFPC, gas flow proportional counter.

ference was taken into account by using a narrow window in the pulse-height analyser. The results of the microprobe analyses are given below.

$HoBa_2Cu_{3-\varepsilon}Al_yO_{7-\delta}$. The Al_2O_3 content of the crystal was 0.77%, and the composition based on 6.5 oxygen atoms in
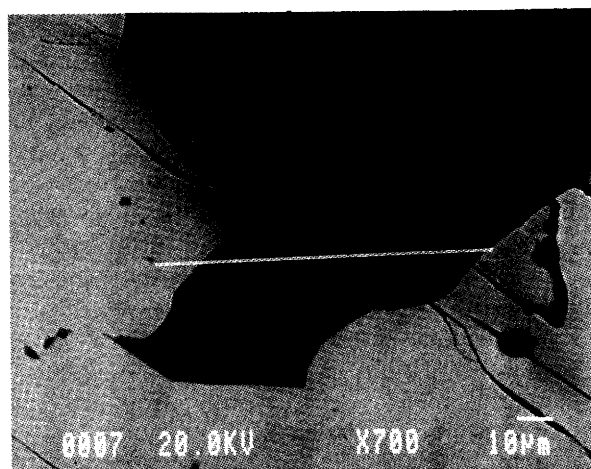

Fig. 1. Back-scattered electron image of inclusion in the $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$ crystal, which appears white; $BaCuO_2$ is grey and CuO is dark grey.
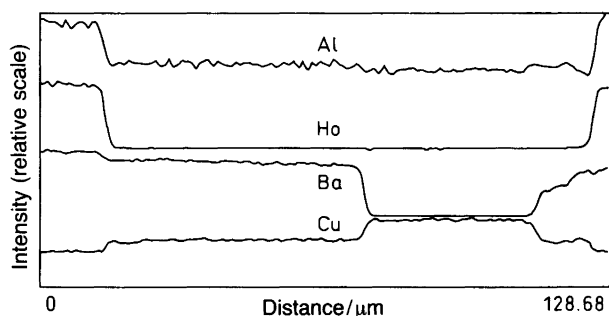
Fig. 2. Distribution of the Cu, Ba, Ho, and Al contents along the line shown in Fig. 1. (The length of the scan is 128.68 μm). The Cu content was measured with an energy-dispersive spectrometer using a Si (Li) detector. Ba, Ho and Al were detected using the wavelength dispersive spectrometers. The aluminium content is highest in the $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$ crystal.

the formula unit was $Ho_{0.966}Ba_{2.093}Cu_{2.792}Al_{0.111}O_{6.5}$. In the microprobe analysis the oxygen content is determined as the difference between the metal atom percentage and 100 %. The number of oxygen atoms in the formula unit, 6.5 atoms (or 6.3 atoms, see below), was derived from the refinements of the neutron diffraction data, omitting the scattering contributions from aluminium. The analyses were made at 25 points on the crystal placed at equidistant spacings of 0.033 mm over the face. No significant deviation in the Al content from the average Al compositions was observed. An inhomogenous irregular area at one end of the crystal was observed. It was ca. 1×0.4 mm² in size and consisted mainly of CuO. A minor part (ca. 0.12×0.12 mm²) of this area is shown in Fig. 1. Fig. 2 displays a line-scan of the Ho, Ba, Al and Cu contents that correspond to the compositions $BaCuO_2$ and CuO. The investigation also showed minor areas in the crystal of composition CuO.

$YBa_2Cu_{3-t}Al_yO_{7-\delta}$. The Al_2O_3 content was found in the same way as described above to be 0.91 %. The composition, based on 6.3 or 6.5 oxygen atoms in the formula unit, was $Y_{1.037}Ba_{1.881}Cu_{2.722}Al_{0.101}O_{6.3}$ or $Y_{1.068}Ba_{1.938}Cu_{2.804}Al_{0.104}O_{6.5}$. The analyses were made at 25 points on the crystal with an equidistant spacing of 0.038 mm over the face. A slight tendency to a higher Al content than the average value of the 25 measurements was observed at one of the edges of the crystal. Almost at the centre of this crystal were observed two inhomogenous areas each of ca. 1.7×0.4 mm². The long sides of the areas were parallel to the long edge of the crystal. CuO was also identified in these inclusions, together with irregular particles consisting of Ba, Cu, Y and Al in varying concentrations. A minor part, ca. 0.30×0.30 mm² of this inclusion, is shown in Fig. 3, and Fig. 4 displays a line-scan of the Y, Ba, Al and Cu contents.

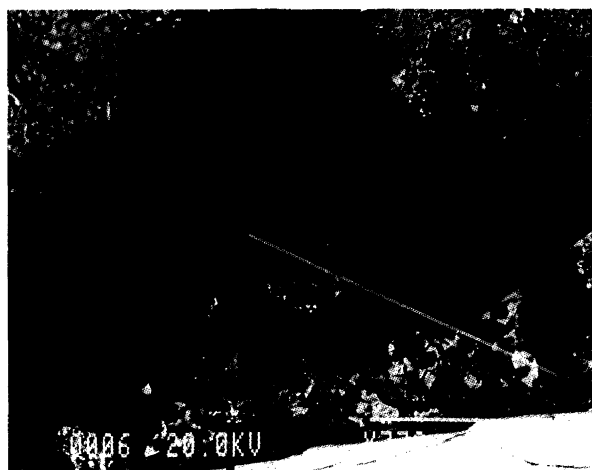Final neutron diffraction analysis of $HoBa_2Cu_{3-t}Al_yO_{7-\delta}$ and $YBa_2Cu_{3-t}Al_yO_{7-\delta}$. It is known from substitution

Fig. 3. Back-scattered electron image of inclusion in the $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31(2)}$ crystal, which appears white in the lower right corner; CuO is grey.
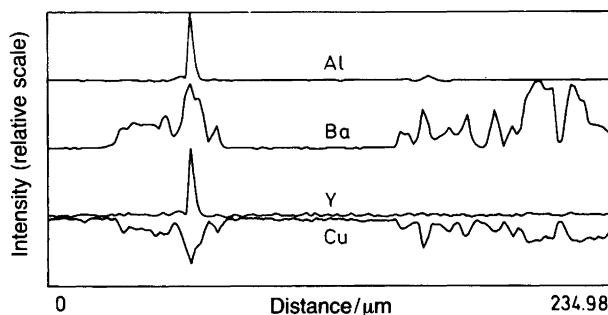

Fig. 4. Distribution of the Cu, Y, Ba and Al contents along the line shown in Fig. 3. (The length of the scan is 234.98 μm). The Cu content was measured with an energy dispersive spectrometer using a Si (Li) detector. Y, Ba and Al were detected using the wavelength dispersive spectrometers.

studies of $YBa_2Cu_3O_7$ that the substituting metal ions first enter at the Cu1 site.[19,20] The final least-squares analysis of the single-crystal neutron diffraction data was made with a fixed aluminium content corresponding to the results from the microprobe analysis placed in site 1a. The model of the structures was then refined (the parameters are listed in Tables 2 and 3), and the compositions found for the two crystals from these analyses were $YBa_2Cu_{2.874(8)}Al_{0.10(1)}O_{6.31(2)}$ and $HoBa_2Cu_{2.890(8)}Al_{0.11(1)}O_{6.53(2)}$, respectively. The standard deviations of the aluminium contents were calculated from the microprobe analysis.

Discussion

The investigation of the copper nonstoichiometry of the tetragonal $REBa_2Cu_3O_{7-\delta}$ single crystals grown in alumina vessels by X-ray diffraction methods indicates a copper occupancy of site 1a of 0.87(1)–0.961(6) (this work and Refs. 6–8) when the presence of the impurity element

aluminium is neglected. A major problem in determining the copper content from diffraction data is the correlation between occupancy and temperature factor parameters in the refinements. However, in the two sets of X-ray data the occupancy and temperature factor of Cu1 were refined simultaneously. The present investigation, as well as that of Ref. 8, shows unambiguously that the crystals of $YBa_2Cu_3O_{7-\delta}$ and $HoBa_2Cu_3O_{7-\delta}$ grown from a BaO–CuO flux have a nonstoichiometry for Cu1. This copper non-stoichiometry may be due to vacancies in site 1a, or some of the 1a sites may have aluminium atoms originating from the crucible material. From the X-ray diffraction data alone it is difficult to determine whether the copper nonstoichio-metry is due to vacancies or to the combination of vacancies and aluminium atoms at some of the copper atoms of site 1a.

The size of the single crystals used in the X-ray analysis precluded a microprobe analysis of the same crystals. For this reason no attempts were made to distinguish between Cu1 nonstoichiometry and a combination of Al substitution and nonstoichiometry for Cu1 for the two sets of X-ray data. However, this was possible with the results from the two crystals used in the neutron diffraction measurements, and for both crystals Cu1 was shown to have Al substitution and thus significant Cu deficiencies in site 1a. However, the Cu/Al occupation of site 1a does not deviate significantly from a fully occupied site according to the analysis.

Cu1 is the copper atom with octahedral coordination at which the oxygen ligands O1 and O4 are mainly responsible for the oxygen nonstoichiometry of the compound. The as-grown crystals are strongly oxygen-deficient at sites 2f and 2g. The oxygen contents of sites 2f and 2g can be increased by annealing the compound in oxygen at ca. 550 °C, and this results in the high-T_c superconducting material with an orthorhombic structure. However, it is not expected that the nonstoichiometry of the copper atom Cu1 will be changed under the applied annealing conditions. The annealed crystals should thus have the same level of Cu deficiency as the as-grown crystals.

References

1. Licci, F., Scheel, H. J. and Besagni, T. *Physica C 153–155* (1988) 431.
2. Sadowski, W. and Scheel, H. J. *J. Less-Common Met. 150* (1989) 219.
3. Kowalewski, J., Nikl, D. and Assmus, W. *Physica C 153–155* (1988) 429.
4. Steinfink, H., Swinnea, J. S., Sui, Z. T., Hsu, H. M. and Goodenough, J. B. *J. Am. Chem. Soc. 109* (1987) 3348.
5. Swinnea, J. S. and Steinfink, H. *J. Mater. Res. 2* (1987) 424.
6. Nakai, I., Sueno, S., Okamura, F. P. and Ono, A. *Jpn. J. Appl. Phys. 26* (1987) L788.
7. Nakai, I., Imai, K., Kawashima, T. and Yoshizaki, R. *Jpn. J. Appl. Phys. 26* (1987) L1244.
8. Roth, G., Heger, G., Schweiss, P., Renker, B., Assmuss, W., Kowalewski, J. and Pannetier, J. *Physica C 152* (1988) 329.
9. Jorgensen, J. D., Veal, B. M., Kwok, W. K., Crabtree, G. W., Umezawa, A., Nowicki, L. J. and Paulikas, A. P. *Phys. Rev. B 36* (1987) 5731.
10. Sakata, M., Kumazawa, S., Takata, M. and Ishida, K. In: Authier, A., Ed., *15th Congress and General Assembly, International Union of Crystallography, July 1990, Bordeaux. Collected Abstracts.* Bordeaux 1990. Abstract No. PS-02.02.09, p. C-44.
11. Arabi, H., Cionartan, D. A., Clamp, M. E., Fenn, R. H., Mills, O. S., Mitchell, P. W., Ross, J. W., Staliford, D. J. and Tao, T. In: Authier, A., Ed., *15th Congress and General Assembly, Internal Union of Crystallography, July 1990, Bor-deaux. Collected Abstracts.* Bordeaux 1990. Abstract No. PS-08.05.07, p. C-316.
12. Inoue, Z., Sasaki, S., Iyi, N. and Takekawa, S. *Jpn. J. Appl. Phys. 26* (1987) L1365.
13. Sonntag, R., Hohlwein, D., Collin, G. and Brückel, T. *Phys. Rev. Lett. 66* (1991) 1497.
14. Christensen, A. N. 13th European Crystallographic Meeting, Ljubljana–Trieste 1991. Book of Abstracts, p. 89.
15. Busing, W. R., Martin, K. O. and Levy, H. A. *ORFLS. A Fortran Crystallographic Least-Squares Program.* Report ORNL-TM 305. Oak Ridge National Laboratory, Oak Ridge, TN 1962. LINUS is a 1971 version of ORFLS.
16. Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A24* (1968) 321.
17. Koester, L. and Rauch, H. *Summary of Neutron Scattering Lengths,* KFA, Jülich, Germany 1981.
18. Drake, M. J. and Weill, D. F. *Chem. Geol. 10* (1972) 179.
19. Sonntag, R., Hohlwein, D., Hoser, A., Prandl, W., Schaefer, W., Kiemel, R., Kernmler-Sack, S., Loesch, S., Schlichenmaier, M. and Hewat, A. W. *Physica C159* (1989) 141.
20. Siegrist, T., Schneemeyer, L. F., Waszczak, J. V., Singh, N. P., Opila, R. L., Batlogg, B., Rupp, L. W. and Murphy, D. W. *Phys. Rev. B36* (1987) 8365.