

Superconducting Cuprates and Related Oxides VII. Self-Nucleation and Top Seeded Crystal Preparation of Cuprates

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Cobalt doped single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and single crystals of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were grown in alumina crucibles from a BaO–CuO flux. The composition of the crystals were determined by microprobe analysis and from neutron single crystal diffractometry. Crystal A: $\text{YBa}_2\text{Cu}_{2.71(2)}\text{Al}_{0.10(1)}\text{Co}_{0.15(1)}\text{O}_{6.51(4)}$. Space group $P4/mmm$ (No. 123), $a = 3.873(1)$, $c = 11.704(2)$ Å. Crystal B: $\text{PrBa}_2\text{Cu}_{2.75(3)}\text{Al}_{0.10(1)}\text{O}_{6.64(10)}$. Space group $P4/mmm$ (No. 123), $a = 3.921(1)$, $c = 11.757(2)$ Å.

The orthorhombic forms of the ternary cuprates $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE = rare earth element, δ close to zero) are the high- T_c materials, with transition to superconductivity in the 80–90 K temperature range. Large single crystals of these ternary cuprates are required for investigation of the physical properties of the high- T_c materials. Several papers describe the crystal growth of ternary cuprates from a BaO–CuO flux, see Refs. 1–7 and references in these articles. The crystals of these cuprates are in general grown as tetragonal and non-superconducting in the 80–90 K temperature range, but transforms on oxidation to orthorhombic high- T_c cuprates. When the crystal growth is performed in a crucible of Al_2O_3 , the flux corrodes the crucible and Al is deposited in the crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. A single-crystal neutron diffraction analysis of such a crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ combined with a microprobe analysis of the same crystal⁸ showed that the composition was $\text{YBa}_2\text{Cu}_{2.874(8)}\text{Al}_{0.10(1)}\text{O}_{6.31(2)}$ and that Al atoms were located in site 1a together with the copper atom Cu1. The microprobe analysis showed also that the crystal investigated contained minor inclusions of BaCuO_2 and of CuO.

It is also possible to substitute some of the copper atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by the transition metal atoms Co and Fe^{9–14} in the solid-state synthesis of polycrystalline samples. Such substitution of copper by cobalt may also be achieved in single-crystal growth. In the crystal growth of ternary cuprates reported in Ref. 7, crucibles of Al_2O_3 were used, and the crystals grew at a slow cooling rate in the temperature range 1000–920 °C.

Crystals were formed by self-nucleation in the flux on the inside wall of the crucible and in the surface layer of the melt. However, the best method to grow large single crystals of the ternary cuprates is by the top-seeded solution growth.^{1–3} In this paper crystal preparation by self-nucleation as well as by top-seeded solution growth is reported.

Experimental

The crystal growth furnace used in the self-nucleation growth was the same as applied previously.⁷ The furnace used in the top-seeded growth is a second generation of the furnace used in Ref. 1. A sketch of the furnace is displayed in Fig. 1. It is a vertical tube furnace with two heating elements controlled by two Eurotherm units. A feeder of the ternary cuprate is placed at the bottom of the crucible and seed crystals are placed just below the surface of the melt. The seed crystals are attached to Al_2O_3 or ZrO_2 crystal holders by platinum wires. The growth temperature was typically 975 °C with a temperature gradient from growing crystal to feeder of 0.7 °C. The distance between the growing crystal and the feeder was typically 2 cm.

The chemicals used were: Y_2O_3 , Auer-Remy, 99.99%, Pr_6O_{11} , Auer-Remy, 99.9%, BaCO_3 , Merck p.a., BaO and CuO, Merck p.a., and BaO_2 , Johnson Matthey, 97.5%, CoCO_3 , Baker Analyzed Reagent. The composition of the reaction mixtures and the experimental conditions for the two crystal preparation modes are listed in Tables 1 and 2. In the self-nucleation growth, the chemicals were mixed carefully in a porcelain mortar and prereacted at 850 °C for 12 h. The mixture was then

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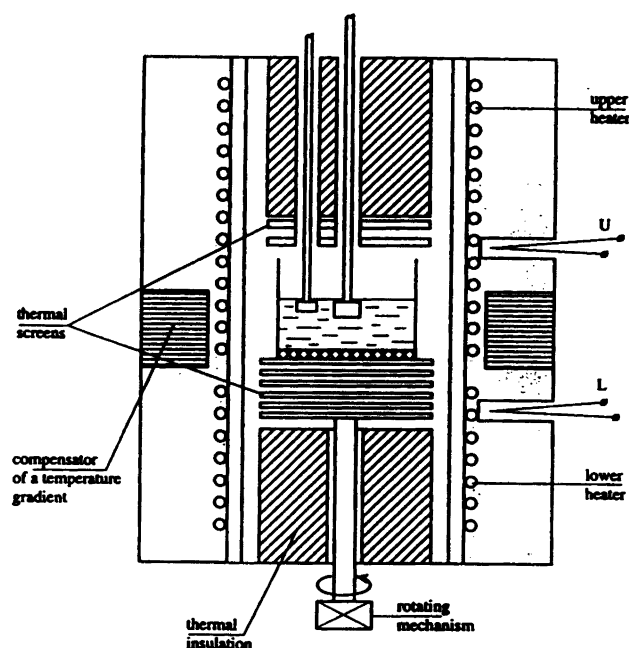


Fig. 1. Sketch of the crystal growth furnace showing two heaters, upper and lower, and the positions of the two thermocouples U and L, to control the power via the two Eurotherm units. The crucible is rotated. One of the Al_2O_3 rods placed in the melt acts as a stirrer and the other rod has the seed crystal mounted.

ground in a porcelain mortar and pressed to pellets at a pressure of 400 MPa in a cemented carbide mould. A pile of the pellets with a diameter 25 mm was placed in the Al_2O_3 crucible in the vertical tube furnace.⁷ The following heating/cooling programme, controlled by a Eurotherm unit, is typical for the growth experiment performed: room temperature to 950 °C with 100 °C h⁻¹; 950 °C for 5 h; 950 to 1010 °C with 5 °C h⁻¹; 1010 °C for 1 h; 1010 to 1009 °C with 1 °C h⁻¹, and 1009 to 920 °C with 0.5 °C h⁻¹. At 920 °C the flux was decanted from the crucible. The flux was removed from the crystals as reported previously.⁷

In the top seeded growth the Al_2O_3 or ZrO_2 crucible was filled with the reaction mixture. Figures 2 and 3 are the temperature profiles of a typical growth experiment recorded on the Eurotherm control units (Fig. 2) and measured in the melt (Fig. 3) below the surface of the melt (A) and above the bottom of the crucible (B). After the melt has been established, the feeder of the ternary cuprate is formed at the bottom of the crucible by lowering the temperature of the melt ca. 100 °C. At the growth conditions a temperature gradient in the melt of 0.3 to 0.8 °C is established and the ternary cuprate material is transported from the feeder to the seed crystals by convection in the melt.

The single crystals obtained in the self-nucleation preparations had typically sizes of $5 \times 5 \times 0.5$ to $8 \times 8 \times 1.5$ mm³. The crystals obtained in the top-seeded growth had typically a volume of 1 cm³. The seed holders (of Al_2O_3 or ZrO_2) were cut from the samples with a

Table 1. Crystal growth conditions for yttrium and rare earth cuprates. Self-nucleation growth mode.

Experiment separation no.	Quantities/g		Mole fraction (%)			Crucible	Soak temp. and time °C/h	Cooling rate °C h ⁻¹	Flux pouring at temp. °C	Flux removed temp. and time/°C/h		
1	Y ₂ O ₃ 3.4	BaCO ₃ 165.8	CuO 164.7	CoCO ₃ 7.1	YO _{1.5} 1.0	BaO 28.0	CuO 69.0	Al ₂ O ₃	1010/1	0.5	920	920/5
2	Y ₂ O ₃ 3.4	BaCO ₃ 165.8	CuO 168.9	CoCO ₃ 0.7	YO _{1.5} 1.0	BaO 28.0	CuO 70.8	Al ₂ O ₃	1010/1	0.5	920	920/5
3	Y ₂ O ₃ 3.4	BaCO ₃ 159.9	CuO 171.8		YO _{1.5} 1.0	BaO 27.0	CuO 72.0	Al ₂ O ₃	1010/1	0.5	920	920/5
4	Y ₂ O ₃ 3.4	BaCO ₃ 162.8	CuO 170.6		YO _{1.5} 1.0	BaO 27.5	CuO 71.5	Al ₂ O ₃	1010/1	0.5	920	920/5
5	Y ₂ O ₃ 3.9	BaO 65.6	CuO 149.2		YO _{1.5} 1.0	BaO 29.0	CuO 70.0	ZrO ₂	1010/1	0.5	920	930/5
6	Pr ₆ O ₁₁ 3.9	BaO 55.3	CuO 135.2		PrO _{1.83} 2.0	BaO 28.4	CuO 69.6	Al ₂ O ₃	1010/1	0.5	930	930/5

Table 2. Crystal growth conditions for yttrium and rare earth cuprates. Top seeded growth mode. Crystal size in most of the experiments 5–10 mm.

Experiment no.	Quantities/g			Mole fraction (%)			Crucible	Soak temp. /°C	Growth temp. /°C	Gradient in crucible /°C		
A2	Y ₂ O ₃ 13.2	BaO ₂ 234.6	CuO 252.2	YO _{1.5} 2.4	BaO 31.5	CuO 66.1	Al ₂ O ₃	1050	975	0.7		
A3	Y ₂ O ₃ 13.5	BaO 212.5	CuO 252.2	YO _{1.5} 2.6	BaO 29.4	CuO 68.1	Al ₂ O ₃	1050	975	0.7		
A5	Pr ₆ O ₁₁ 16.4	BaO 214.6	CuO 268.8	PrO _{1.83} 2.0	BaO 28.4	CuO 69.6	Al ₂ O ₃	1050	975	0.7		
A6	Pr ₆ O ₁₁ 6.4	Y ₂ O ₃ 4.2	BaO 160.5	CuO 201.0	PrO _{1.83} 1.0	YO _{1.5} 1.0	BaO 28.4	CuO 69.5	Al ₂ O ₃	1050	975	0.7
A7	Pr ₆ O ₁₁ 6.4	Y ₂ O ₃ 4.2	BaO 160.5	CuO 201.0	PrO _{1.83} 1.0	YO _{1.5} 1.0	BaO 28.4	CuO 69.5	Al ₂ O ₃	1050	975	0.7
A8	Y ₂ O ₃ 4.7	BaO 114.0	CuO 144.4	YO _{1.5} 1.6	BaO 28.6	CuO 69.8	Al ₂ O ₃	1050	975	0.7		
A9	Y ₂ O ₃ 5.3	BaO 114.0	CuO 144.4	YO _{1.5} 1.8	BaO 28.5	CuO 69.7	ZrO ₂	1050	975	0.7		
A10	Y ₂ O ₃ 5.3	BaO 114	CuO 144.4	YO _{1.5} 1.8	BaO 28.5	CuO 69.7	ZrO ₂	1050	975	0.7		

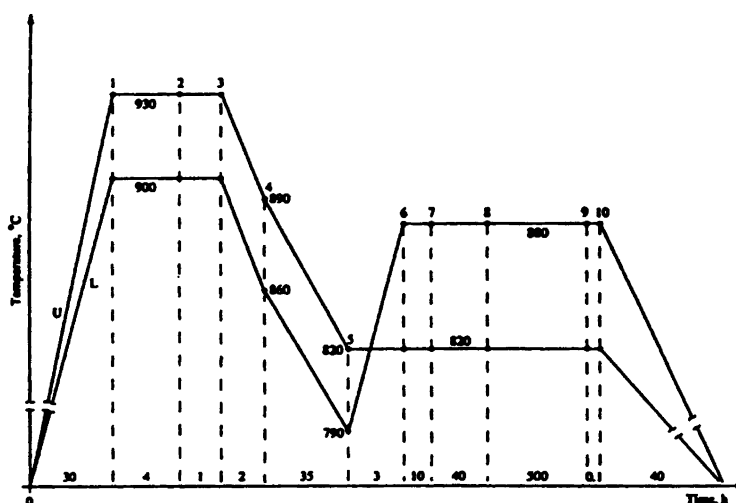


Fig. 2. Sketch of the temperature–time profile recorded with the two thermocouples U and L. In the first part of the growth experiment $U > L$, so that solid $YBa_2Cu_3O_{7-8}$ is deposited in a layer at the bottom of the crucible. During the second part of the growth experiment, $L > U$.

diamond blade yielding single crystals of the cuprates with typical volumes of 0.3 cm^3 .

Characterization

Crystals from the self-nucleation growth. The content of cobalt and aluminium in crystals from the growth experiment to produce cobalt-doped $YBa_2Cu_3O_{7-8}$ crystals was determined by microprobe analysis. Two crystals from the same growth experiment (No. 2) were selected and 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 soft-ware TASK for instrument control and PRZ (atomic number, absorption and fluorescence) corrections. The instrument has a focal spot

of ca. $2 \mu\text{m}$. Wavelength analysis of the X-rays emitted from the sample was carried out with flow-proportional counters using 90% Ar and 10% CH_4 and sealed Xe proportional counters. The following spectral lines and standards were used in the analysis: $YL\alpha$: synthetic glass standard REE3 containing 4.08% Y_2O_3 ; $BaL\alpha$ baryte, BaSO_4 ; $\text{CuK}\alpha$: Cu (metal); $\text{AlK}\alpha$: synthetic Al_2O_3 ; $\text{CoK}\alpha$: Co (metal). The $\text{AlK}\alpha$ line is close to the third-order $\text{BaL}\alpha$ line, but this interference was taken into account by using a narrow window in the pulse-height analyser. The result of the microprobe analysis (based on 6.64 oxygen atoms in the formula unit) gave an average composition of the cuprate crystals as $\text{Y}_{1.06(1)}\text{Ba}_{1.99(2)}\text{Cu}_{2.75(2)}\text{Co}_{0.15(1)}\text{Al}_{0.09(1)}\text{O}_{6.64}$. In the microprobe analysis the oxygen content is not measured, but calculated on the basis of the metal content. The real

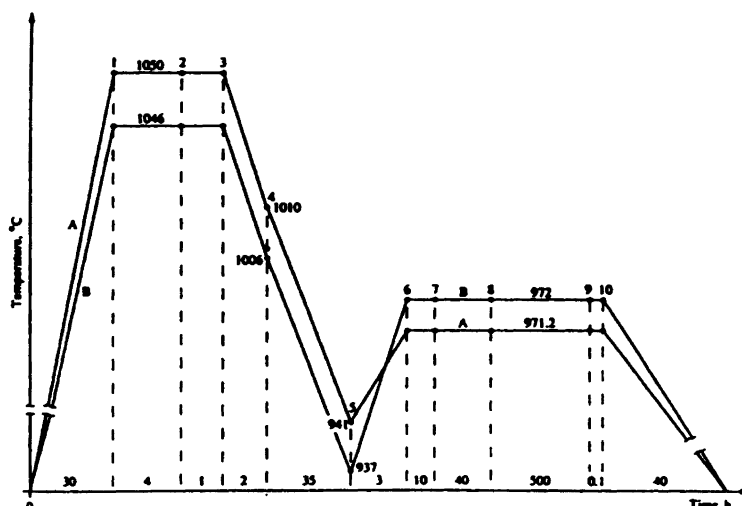


Fig. 3. Sketch of the temperature-time profile measured in the melt below the surface of the melt (A), and above the bottom of the melt (B). During the long growth period (500 h) the two thermocouples are not placed in the melt. The numbers above the curve indicate the following: 0-1: The loosely packed reaction mixture is heated and is completely melted at 1, $U > L$ (see Fig. 2). 1-2: Temperatures (A) and (B) are measured with thermocouples. 2-3: Al_2O_3 rod is introduced in the melt, the crucible is rotated and the melt is thus stirred. 3-4-5: Stirring is continued, the temperature is reduced, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ feeder material is deposited on the bottom of the crucible. 5-6-7: Stirring is stopped and the Al_2O_3 rod is removed. Temperature is adjusted to $L > U$. 7-8: Temperature measured with thermocouples, $B > A$, an adjusted to $B-A = 0.7-0.8^\circ\text{C}$. 8-9: Seed crystals placed below surface of melt and crucible rotated. 9-10: Seed crystals withdrawn from the melt and slowly withdrawn from the furnace. Power to the furnace is cut.

oxygen content in the formula most likely does not exceed the value 6.5. The Cu, Co and Al atoms most likely completely fill the $1a$ and $2g$ sites in the structure. It is not clear why the number of Y atoms in the analysis is significantly larger than 1.0.

The two crystals investigated both had a large inclusion of CuO in their cores. The dimensions of the two inclusions were $1.6 \times 0.02 \text{ mm}^2$ and $2.0 \times 0.04 \text{ mm}^2$, compared with values of $3.0 \times 0.6 \text{ mm}^2$ and $6.0 \times 0.5 \text{ mm}^2$ for the crystal edges, respectively. The crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ apparently grew on a seed crystal of CuO.

Single-crystal neutron diffraction analysis of a crystal of $\text{YBa}_2\text{Cu}_{3-\epsilon}\text{Al}_\gamma\text{Co}_\beta\text{O}_{7-\delta}$. A single crystal (from experiment no. 2) with the dimensions $6.0 \times 6.0 \times 0.8 \text{ mm}^3$ was used in the diffraction measurements. The data were measured on a Huber four-circle diffractometer at DR3, Risø National Laboratory, using a neutron wavelength of 1.013 \AA . A total of 3598 reflections, including two standard reflections for every 50 reflections, were measured in a sphere with the Miller-index limits $-5 \leq h \leq 5$, $-5 \leq k \leq 5$, $-16 \leq l \leq 16$. A Gaussian integration with $\mu = 0.064 \text{ cm}^{-1}$ was applied in an absorption correction, yielding a transmission range 0.971-0.995. After taking averages of the symmetry related reflections, the number of independent reflections with $I > 3\sigma(I)$ was 334. The R -values on averaging were $R = 5.9\%$, and $R_w = 6.7\%$.

The model of the structure was refined using the least-squares program LINUS¹⁶ with atomic scattering lengths from Ref. 17. Starting parameters for the model were taken from Ref. 8, and the final R -value obtained was

5.5%. The values of the refined parameters are listed in Table 3.

Single-crystal neutron diffraction analysis of a crystal of $\text{PrBa}_2\text{Cu}_{3-\epsilon}\text{Al}_\gamma\text{O}_{7-\delta}$. A single crystal (from experiment No. 6) with the dimensions $6.0 \times 6.0 \times 0.8 \text{ mm}^3$ was used in the diffraction measurements using the same diffractometer as above and 1.012 \AA neutrons. The reflection in a sphere with the Miller-index limits $-5 \leq h \leq 5$, $-5 \leq k \leq 5$, $-16 \leq l \leq 16$ gave 3280 reflections, including 3 standard reflections for every 50 reflections. Absorption corrections calculated as above with $\mu = 0.080 \text{ cm}^{-1}$ showed a transmission range 0.964-0.994. The average of symmetry-related reflections

Table 3. Refined parameters from the single-crystal neutron diffraction analysis of $\text{YBa}_2\text{Cu}_{2.71(2)}\text{Al}_{0.10(1)}\text{Co}_{0.15(1)}\text{O}_{6.51(4)}$.^a

Atom	Site	A^b	x/a	y/b	z/c	$B/\text{\AA}^2$
Y	1d	1.0	1/2	1/2	1/2	0.61(4)
Ba	2h	2.0	1/2	1/2	0.1920(3)	0.89(5)
Cu1	1a	0.71(2)	0	0	0	1.08(10)
Al	1a	0.10(1)	0	0	0	1.08(10)
Co	1a	0.15(1)	0	0	0	1.08(10)
Cu2	2g	2.0	0	0	0.3606(2)	0.68(4)
O1	2g	1.91(3)	0	0	0.1532(3)	1.75(8)
O2	4i	4.0	0	1/2	0.3783(2)	0.81(4)
O3	2f	0.61(4)	0	1/2	0	3.13(39)

^a Space group $P4/mmm$ (No. 123). Unit-cell parameters: $a = 3.873(1)$, $c = 11.704(2) \text{ \AA}$. $R = 5.5\%$, $R(w) = 4.9\%$. Isotropic extinction parameter: 0.00059(4). ^b Wyckoff number times occupancy.

gave 329 reflections with $I > 3\sigma(I)$, and the R -values on the averaging were $R = 11.1\%$ and $R_w = 9.4\%$. The model calculation performed as above gave a final R -value of 8.8% . The values of the refined parameters are listed in Table 4.

Crystals from the top-seeded growth. The top-seeded growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in Al_2O_3 crucibles gave crystals of up to 1 cm^3 volume. Smaller samples of crystals were cut from these crystals to remove the seed holders of Al_2O_3 or ZrO_2 , and were used in neutron diffraction investigations.¹⁸ Crystal preparation from ZrO_2 crucibles was more difficult than from the Al_2O_3 crucibles. The melt had a tendency to creep up on the inside of the crucible and the feeder of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ did not deposit on the bottom of the crucible. X-Ray powder patterns taken of the frozen melt that had a height of 2 cm showed the following compounds: At the melt surface the melt had frozen to BaCuO_2 and CuO ; at the bottom the frozen solids were Ba_2CuO_3 and CuO and ca. 8 mm from the bottom the solid was $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The growth experiment with the ZrO_2 crucible gave a slow growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and a poor quality.

Discussion

The local Co–Cu ordering in a single crystal with the composition $\text{YBa}_2\text{Cu}_{2.53}\text{Co}_{0.47}\text{O}_{7.13}$, recently studied with anomalous diffuse X-ray scattering, indicate that the Co and Cu atoms are nearly randomly distributed on the Cu1 site.¹⁹ The crystal used was grown from a ZrO_2 crucible and did not contain any contamination from the crucible. The investigation indicated a domain distribution of Co and Cu atoms in the Cu1 site with Co-free domains of the size of $5\text{--}7\text{ \AA}$, and indicated a significant decrease of the Co–O1 distance compared to the Cu–O1 distance, thus leading to an increase of the Cu2–O1 distance which implies a lowering of the Cu2 formal valence.¹⁹ Such a detailed model cannot be argued based on the present single-crystal structure analysis of the Co-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystal. The atomic coordinates reported for the structure of $\text{YBa}_2\text{Cu}_{2.71(2)}\text{Al}_{0.10(1)}\text{Co}_{0.15(1)}\text{O}_{6.51(4)}$ (Table 3) are not significantly different from the atomic coordinates reported for $\text{YBa}_2\text{Cu}_{2.874(8)}\text{Al}_{0.10(1)}\text{O}_{6.31(2)}$ in Ref. 8, and a significant shortening of the distance from the Cu1 site to O1 is not apparant. The Co content in the crystal investigated in this work is approximately 1/3 of the Co content of the crystal investigated in Ref. 19. The positional parameters arrived at for the Pr-cuprate (Table 4) are not significantly different from those found for a reduced Pr-cuprate crystal in a single-crystal neutron diffraction analysis.¹⁸

The compositions of the two crystals investigated by single-crystal neutron diffraction analysis were arrived at in the following way: Y, Pr, and Ba were assumed to have the coefficients one, one and two, respectively, in

Table 4. Refined parameters from the single-crystal neutron diffraction analysis of $\text{PrBa}_2\text{Cu}_{2.75(3)}\text{Al}_{0.10(1)}\text{O}_{6.84(10)}$.^a

Atom	Site	A^b	x/a	y/b	z/c	$B\text{\AA}^2$
Pr	1d	1.0	1/2	1/2	1/2	0.85(10)
Ba	2h	2.0	1/2	1/2	0.1867(4)	1.15(7)
Cu1	1a	0.75(3)	0	0	0	1.84(16)
Al	1a	0.10(1)	0	0	0	1.84(16)
Cu2	2g	2.0	0	0	0.3513(2)	0.84(5)
O1	2g	1.89(5)	0	0	0.1517(6)	3.22(16)
O2	4i	4.0	0	1/2	0.3688(2)	0.95(5)
O3	2f	0.75(5)	0	1/2	0	2.31(34)

^a Space group $P4/mmm$ (No. 123). Unit cell parameters: $a = 3.921(1)$, $c = 11.757(2)\text{ \AA}$. $R = 8.8\%$, $R(w) = 5.1\%$. Isotropic extinction parameter: $0.00033(4)$. ^b Wyckoff number times occupancy.

the formulae. Al and Co (Table 3) were given the coefficients 0.10 and 0.15, respectively, which are values close to the results of the microprobe analysis. The oxygen content was then calculated from the occupancies of the three oxygen atoms. For the Pr-cuprate (Table 4) the coefficient of Al was set to 0.10. This crystal was grown in the same way as the Y-cuprate (Table 2). However, a microprobe analysis of the Pr-cuprate was not made.

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