and 1·75 (3) Å, in accord with values found in other Re$^{VII}$ compounds, e.g. Pb(ReO$_4$)$_2$ where the distances range from 1·65 (5) to 1·84 (6) Å (Picard, Baud, Besse & Chevalier, 1984). The IR spectrum shows the characteristic $\nu_1$(ReO$_4^-$) tetrahedral stretching vibrations at 900 and 913 cm$^{-1}$. It is most probable that the OH groups form hydrogen bonds to neighbouring oxygens of the ReO$_4^-$ groups; the distances of these contacts range from 2·92 (3) to 3·07 (3) Å, and in the IR spectrum the (OH) vibrations occur between 3600 and 3300 cm$^{-1}$. The water molecule is remote from the metal atoms. Its nearest oxygen neighbours are O(14) at 2·74 Å and O(4) at 2·86 Å, suggesting hydrogen bonding here, too. The other oxygens are at distances of 3·26 Å or more. The lattice parameters of Pb$_6$O(OH)$_6$(ReO$_4$)$_4$.H$_2$O are superficially related to those of α-Pb$_6$O(OH)$_6$-(ClO$_4$)$_4$.H$_2$O [*Pbca*; $a = 10\cdot814$, $b = 16\cdot706$, $c = 26\cdot273$ Å; Spiro, Templeton & Zalkin (1969)] and the corresponding β-phase [*Pbca*; $a = 19\cdot953$, $b = 17\cdot624$, $c = 13\cdot383$ Å; Olin & Söderquist (1972)], but the arrangement of the Pb$_6$O(OH)$_6^{4+}$ and XO$_4^-$ units is entirely different in the rhenium compound.

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# Structure of High-$T_c$ Superconducting Tetragonal Ba$_2$YCu$_{3-x}$O$_{7-y}$ at 298 and 120 K

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**Abstract.** A high-$T_c$ superconductor, Ba$_2$YCu$_{3-x}$O$_{7-y}$ [$x = 0\cdot130$ (5), $y = 0\cdot24$ (4)], $M_r = 654\cdot1$, tetragonal, space group *P4/mmm*, $Z = 1$, Ag *K*α ($\lambda = 0\cdot56087$ Å), $F(000) = 288\cdot3$. (i) At $T = 298$ K, $a = 3\cdot8683$ (6), $c = 11\cdot688$ (2) Å, $V = 174\cdot89$ (6) Å$^3$, $D_x = 6\cdot21$ Mg m$^{-3}$, $\mu$(Ag *K*α) = 14·8 mm$^{-1}$, $R = 0\cdot029$ (427 unique reflections). (ii) At $T = 120$ K, $a = 3\cdot8609$ (5), $c = 11\cdot645$ (2) Å, $V = 173\cdot60$ (5) Å$^3$, $D_x = 6\cdot25$ Mg m$^{-3}$, $\mu = 14\cdot9$ mm$^{-1}$, $R = 0\cdot032$ (417 unique reflections). The crystal consists of triple layers of oxygen-deficient perovskite-like structure with a linear arrangement of −Ba−Y−Ba− along **c**. In the layer sandwiched between two Ba layers, there are marked deficiencies of Cu and O ions; the valence state of the Cu ion is +3; moreover, the temperature factors of the oxygen ions are very high.

**Introduction.** Since the discovery of high-$T_c$ superconductivity in a Ba−Y−Cu−O compound system (Wu *et al.*, 1987), many reports characterizing the superconducting properties have been presented (Cava *et al.*, 1987; Batlogg *et al.*, 1987). The crystal is tetragonal at temperatures higher than about 853 K (Sueno, Nakai, Okamura & Ono, 1987). At room temperature

it is either tetragonal or orthorhombic depending on the conditions of cooling after sintering at higher temperatures. Structures determined by the X-ray diffraction method using very small single crystals have been reported (Hazen *et al.*, 1987; LePage, McKinnon, Tarascon, Greene, Hull & Hwang, 1987; Siegrist, Sunshine, Murphy, Cava & Zahurak, 1987; Okamura, Sueno, Nakai & Ono, 1987; Nakai, Sueno, Okamura & Ono, 1987). The structures reported basically agree with each other except for the oxygen content. We have prepared high-quality single crystals with dimensions of several hundred micrometres and reported a preliminary result of the structure analysis (Sato, Nakada, Kohara & Oda, 1987). Further details are given in this paper.

**Experimental.** The crystals were prepared from a pressed pellet of mixed $BaCO_3$, $Y_2O_3$ and $CuO$ in molar ratio 4:1:5. It was sintered in the air at 1223 K for one day. A crystal having well developed {001} faces was cut to a plate with dimensions $0.24 \times 0.20 \times 0.10$ mm. Intensities of Bragg reflections were measured on an automated Rigaku AFC-3 four-circle diffractometer at 298 and 120 K, graphite-monochromated Ag $K\alpha$. A rough measurement was also made at 90 K. $\omega$-scan, scan range $2\theta < 70°$, scan width $\Delta\omega = (2.3 + 0.5\tan\theta)°$, $[(\sin\theta)/\lambda]_{max} = 1.02$ Å$^{-1}$, scan speed 2°min$^{-1}$, 1318 reflections with $|F_o| > 3\sigma(|F_o|)$ observed at 298 K ($h = -7 \rightarrow 7$, $k = 0 \rightarrow 7$ and $l = 0 \rightarrow 23$; 427 unique, 540 possible, $R_{int} = 0.026$). To examine the change of thermal parameters $+h +k +l$ reflections measured at 120 K ($2\theta_{max} = 70°$, 719 reflections, 417 unique, $R_{int} = 0.024$); the crystal was cooled by regulated cold nitrogen gas. Lp correction; correction for absorption by the numerical integration method (Busing & Levy, 1957), transmission factor 0.08–0.22. Five standard reflections monitored every 50 reflections showed no significant intensity fluctuation. Cell dimensions were determined by least-squares calculations on the basis of $\theta$ values ($20 < \theta < 22.5°$) of 29 reflections.

This ceramic crystallizes in both orthorhombic and tetragonal systems, probably according to slight differences in its sintering conditions. Diffraction pattern of the present crystal showed the Laue symmetry 4/*mmm*; the observed profiles of 600 and 060 reflections ($2\theta = 50.8°$) and that of 440 ($2\theta = 48°$) had almost the same full width at half maximum, 0.4°; the powder diffraction pattern also indicated tetragonality. Therefore, the space group P4/*mmm* was selected. [As a check of possible slight deviation to lower symmetry, a trial structure refinement with the space group P4 was attempted; it converged to very similar atomic coordinates and to nearly the same $R$ value (0.0005 lower); a significance test on the $R$ factor (Hamilton, 1965) was not applied.]

The positions of Ba, Y and Cu atoms were determined from the Patterson maps. The O atoms

were located from the subsequent Fourier maps. The structure was refined by the full-matrix least-squares method introducing anisotropic temperature factors. The isotropic extinction parameter was also included. At a later stage of the refinement, it was found that Cu and O atoms had relatively large thermal parameters; therefore, their populations were also refined. The thermal parameters of O(2) (see Fig. 1), especially $U_{22}$, were very large. Positional disorder of atoms often causes such large temperature factors. A structure refinement assuming a statistical distribution of this atom at two sites, say at $\frac{1}{2}$, $+\delta$, 0 in which the initial value of $\delta$ was 0.07, was thus attempted; it did not converge. Difference Fourier maps using $F_c$ values without O(2) showed residual electron density centered at $\frac{1}{2}$,0,0. Furthermore, the structure at 120 K reasonably reduced the thermal factors. Thus the disordered arrangement of O(2) was safely rejected. The split maxima of O(2) that appeared in the Fourier maps as stated in a previous paper (Sato *et al.*, 1987) might be due to the termination of the Fourier series.

To check a possible superlattice structure with doubled $a$, some reflections with half-integer $h$ (and $k$) were measured on the diffractometer. The X-ray photographs were also examined carefully. However, no superlattice reflections were detected.
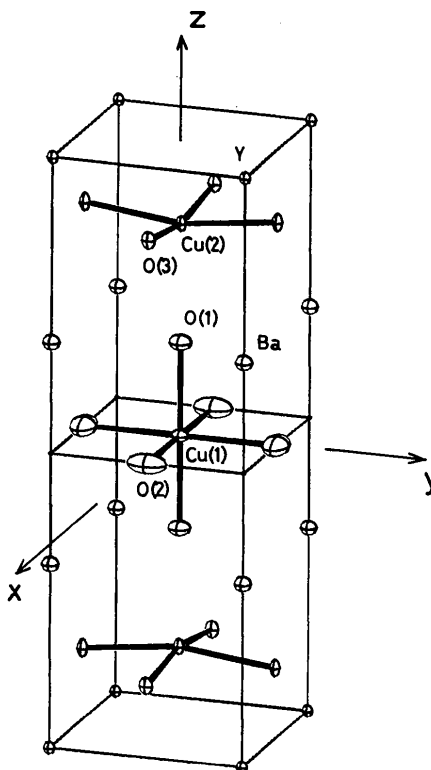


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the structure at 298 K with thermal ellipsoids at the 50% probability level and the numbering scheme of the atoms. Bonds shorter than 2 Å are shown. The boundaries are $\pm a/2$, $\pm a/2$ and $\pm c/2$.

Function minimized $w(|F_o| - |F_c|)^2$, $w = [\sigma^2(|F_o|)$ $+ (0.035|F_o|)^2]^{-1}$. In the following, the former are the values at 298 and the latter at 120 K. Final $R = 0.029, 0.032$; $wR = 0.031, 0.035$; $S = 1.14, 1.26$; secondary-extinction parameter $g = 0.10$ (1), $0.12$ (1) $\times 10^{-4}$; $(\Delta/\sigma)_{max} = 0.12$, $0.15$ for the $z$ parameter of the Ba atom; $\Delta\rho_{max} = 3$, $3\,e\,\text{Å}^{-3}$ near the Ba atom. The atomic occupancies at 120 K were fixed to those at 298 K.

A rough check by means of continuous $\omega$–$2\theta$ scans of $h00$, $hh0$ and $00l$ reflections at 90 K revealed no indication of structural change, such as the generation of superlattice reflections or line broadening.

Atomic scattering factors for $\text{Ba}^{2+}$, $\text{Y}^{3+}$ and $\text{Cu}^{2+}$, and $f'$, $f''$ values taken from *International Tables for X-ray Crystallography* (1974); for $\text{O}^{2-}$ values of Tokonami (1965) were used. The calculations were performed on a FACOM M-380R computer at ISSP, the University of Tokyo; programs used were *UNICS* (Sakurai, 1967), *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) and local programs prepared at ISSP.

**Discussion.** Final atomic parameters are listed in Table 1.* Fig. 1 shows a drawing of the crystal structure. Selected interatomic distances and bond angles are in Table 2.

The crystal is approximately constructed by triple layers of perovskite-like structure in which some atoms are totally or partially deficient. No O atom is located connecting two Cu(2) atoms above and below the mirror plane $z = \frac{1}{2}$. This is the main difference from the perovskite structure. The occupancies of Cu(1), O(1) and O(2) are less than unity, especially that of O(2), which is nearly one half. Around Cu(1), the atomic arrangement is very close to that of perovskite: Cu(1) is octahedrally surrounded by six O atoms and hexahedrally by eight Ba atoms located further apart. As is clear from the interatomic distances given in Table 2, the octahedron is tetragonally compressed, indicating Jahn–Teller distortion: the two Cu–O bonds are about $0.1$ Å shorter than the other four. Four O atoms, O(3) and its equivalents, are bonded to Cu(2); O(3) is also bonded to both Ba and Y, but closer to Y, reflecting the difference in ionic radii between $\text{Ba}^{2+}$ and $\text{Y}^{3+}$. Hence, the coordination plane of the O atoms around Cu(2) is square planar but pyramidally deformed: Cu(2) is shifted about $0.2$ Å away from the basal plane. A much longer Cu(2)–O(1) bond is additionally formed in the apical direction. The Cu(2) and O(3) atoms form a two-dimensional network; the network is puckered; two

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44327 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters with estimated standard deviations in parentheses (upper values of $z$ and $U_{eq}$: 298 K, lower ones: 120 K)*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

| | Occupancy | x | y | z | $U_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|---|
| Ba | 1 | ¼ | ¼ | 0.18791 (2) | 0.0102 (1) |
| | | | | 0.18784 (3) | 0.0065 (1) |
| Y | 1 | ¼ | ¼ | ¼ | 0.0048 (1) |
| | | | | | 0.0023 (2) |
| Cu(1) | 0.870 (5) | 0 | 0 | 0 | 0.0088 (3) |
| | | | | | 0.0054 (3) |
| Cu(2) | 1 | 0 | 0 | 0.35861 (5) | 0.0055 (1) |
| | | | | 0.35843 (7) | 0.0027 (2) |
| O(1) | 0.90 (2) | 0 | 0 | 0.1573 (3) | 0.016 (1) |
| | | | | 0.1568 (5) | 0.013 (1) |
| O(2) | 0.48 (2) | ¼ | 0 | 0 | 0.034 (6) |
| | | | | | 0.026 (7) |
| O(3) | 1 | ¼ | 0 | 0.3779 (2) | 0.0077 (6) |
| | | | | 0.3777 (3) | 0.0045 (7) |

Table 2. *Interatomic distances (Å) and bond angles (°)*

| | | 298 K | 120 K |
|---|---|---|---|
| Ba–O(1) | (×4) | 2.7586 (8) | 2.7539 (8) |
| Ba–O(2) | (×4) | 2.9265 (4) | 2.9174 (4) |
| Ba–O(3) | (×4) | 2.945 (2) | 2.935 (3) |
| Y–O(3) | (×8) | 2.404 (1) | 2.399 (2) |
| Cu(1)–O(1) | (×2) | 1.839 (4) | 1.826 (6) |
| Cu(1)–O(2) | (×4) | 1.9341 (3) | 1.9304 (2) |
| Cu(2)–O(1) | | 2.353 (4) | 2.348 (6) |
| Cu(2)–O(3) | (×4) | 1.9472 (4) | 1.9434 (5) |
| Ba–Y | | 3.6477 (7) | 3.6351 (7) |
| Ba–Cu(1) | (×4) | 3.5079 (4) | 3.4983 (4) |
| Ba–Cu(2) | (×4) | 3.3856 (5) | 3.3763 (6) |
| Y–Cu(2) | (×8) | 3.1958 (4) | 3.1892 (5) |
| Cu(2)–Cu(2i) | | 3.305 (1) | 3.297 (2) |
| O(1)–O(2) | (×4) | 2.669 (2) | 2.657 (4) |
| O(2)–O(2ii) | (×4) | 2.7353 (3) | 2.7301 (2) |
| O(3)–O(3ii) | (×4) | 2.7353 (3) | 2.7301 (2) |
| O(3)–Cu(2)–O(3ii) | | 89.23 (1) | 89.24 (2) |
| O(3)–Cu(2)–O(3iii) | | 166.70 (4) | 166.74 (5) |

Key to symmetry operations: (i) $x, y, 1-z$; (ii) $y, x, z$; (iii) $-x, -y, z$.

such networks in mirror images to each other sandwich the Y atoms. The Y–O distance is quite normal.

A negative excess formal charge is evaluated from the observed copper and oxygen contents and the valence states assumed as $\text{Ba}^{2+}$, $\text{Y}^{3+}$, $\text{Cu}^{2+}$ and $\text{O}^{2-}$: $-13.52$ and $+12.74$ e in a unit cell. If the Cu(1) atom takes the trivalent state, the positive charge becomes $+13.61$ and is almost equally balanced with the negative one. Although the accuracy of the oxygen content is rather limited because of the lowest scattering power of the O atom among the constituent atoms, this charge balance, along with the tetragonal compression of the coordination octahedron around the Cu(1) atom, strongly suggests that Cu(1) is trivalent and that it takes a low-spin $d^8$ configuration in the tetragonal ligand field where the $dz^2$ level is the highest. A trivalent state of the Cu ion is also reported for crystals such as $\text{SrLaCuO}_4$ (Goodenough, Demazeau, Pouchard & Hagenmuller, 1973) and $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$ (Er-Rakho,

Michel, Provost & Raveau, 1981). [The content of the oxygen atoms can be artifically varied to keep the charge balance; this constrained refinement was also tried; it converged to almost the same, but slightly larger $R$ value and to the occupancies Cu(1) 0·887 (5), O(1) 0·80 (1) and O(2) 0·39.]

The temperature factors of O(2) show the extreme anisotropy seen in Fig. 1; the amplitude of the thermal vibration is very large in the direction perpendicular to the Cu—O bond and in the (001) plane [$U_{22}$ of O(2) is 0·063 (4) and 0·042 (10) Å² at 298 and 120 K, respectively]. The structure reported by Nakai et al. (1987), by contrast, showed that the thermal ellipsoid of this atom was elongated perpendicular to the (001) plane; this point as well as the occupancies of O(1) and O(2) differs from the present result. The bondings of O(2) to Cu and Ba might be very weak and easily removed; this bonding character would be reflected in the large values of the thermal parameters and in its low site occupancy.

The thermal parameters are reasonably lower at 120 K as mentioned above. The cell parameters and bond lengths at 120 K are all slightly shorter than those at 298 K. These facts and the experimental results at 90 K suggest no structural change from 298 down to 90 K.

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# Zr₃Rh₅ with Pu₃Pd₅-Type Structure, a Structure Geometrically Related to the CsCl Type

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**Abstract.** $M_r = 788·2$, orthorhombic, Cmcm, $a = 8·6634$ (9), $b = 6·9860$ (3), $c = 8·6218$ (3) Å, $V = 521·81$ (5) Å³, $Z = 4$, $D_x = 10·03$ Mg m⁻³, $\lambda$(Mo $K\alpha$) $= 0·71073$ Å, $\mu = 20·3$ mm⁻¹, $F(000) = 1380$, $T = 293$ K, $R = 0·052$ for 371 independent reflections. The structure of Zr₃Rh₅ can be derived from ZrRh with the