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$YBa(Cu_{1.10}Co_{0.90})O_5$, Prepared from $YBa_2Cu_3O_7$

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Abstract

The title compound, yttrium barium copper cobalt oxide, was grown from $YBa_2Cu_3O_7$ crystals by a modified flux method. The 1,1,2 (Y:Ba:Cu,Co shared) structure is closely related to the parent 1,2,3 structure. The apical O atom in the distorted square pyramid is closer to the Cu,Co site [2.008 (1) Å] than in the parent compound, reflecting the higher average oxidation state, while the basal O atoms are further from the Ba^{2+} cation [3.057 (2) Å].

Comment

Many studies performed on the use of dopants such as Co, Fe, Ni, Zn, Cr and Al in high-temperature superconductors have been aimed at understanding the structural changes, antiferromagnetic and electronic properties of the materials (see, for example, Westerholt *et al.*, 1989) as well as the effect of electronic scattering. We chose to start from high-quality single crystals of known composition, namely the 1,2,3 compound $YBa_2Cu_3O_{7-x}$ (YBCO). Single crystals of a 1,1,2 structure [$YBa(Cu_{1.10}Co_{0.90})O_5$] were grown by a modified flux growth method; details of the synthesis and initial characterization are given by Lin *et al.* (1991). A recent report of this 'new' 1,1,2 phase, with composition $YBaMn_2O_5$, is given by Attfield *et al.* (1996).

The four layer BaO–$(Cu,Co)O_2$–Y–$(Cu,Co)O_2$ structure of the title compound was determined at 124 K and confirms that proposed by Lin *et al.* (1991). The relationship to the parent 1,2,3 YBCO structure, namely, formation by removal of one BaO layer and the so-called CuO 'chain' layer, is illustrated in Fig. 1.

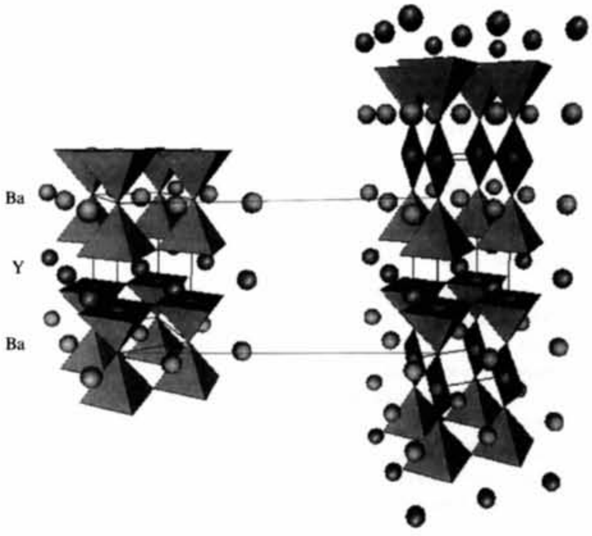

Fig. 1. View showing the relationship between the unit cells of $YBa(Cu_{1.10}Co_{0.90})O_5$ and 'parent' $YBa_2Cu_3O_7$ (Fischer *et al.*, 1990) with the *c* axis vertical. O atoms (not shown) are at the corners of the shaded square pyramids around the mixed Cu,Co sites.

The mixed-site Cu,Co atoms (with *4mm* symmetry) bind five O atoms forming a distorted square pyramid with the Cu,Co atoms 0.354 (3) Å from the basal plane. The Cu,Co—O distances are much closer to each other [1.9733 (7) × 4, 2.008 (1) Å] than those observed in the parent YBCO structure: for the latter in a typical *Pmmm* structure (Francois *et al.*, 1988) the values are 1.923 (1), 1.958 (1), 2.283 (2) Å at 110 K and for a high-temperature P4/*mmm* structure at 373 K (Hewat *et al.*, 1987) they are 1.944 (0) and 2.503 (5) Å. This move to a more regular square-pyramidal geometry is also suggested by values of 1.93 and 2.09 Å used by Geremia *et al.* (1989) for the pure cobalt 1,2,3 modelling. The shortening of the apical oxygen bond length reflects the higher average oxidation state at the mixed Cu^{II},Co^{III} site. There is also a concomitant lengthening of the 12-coordinate Ba—O(basal plane) distances [3.057 (2) Å × 8], compared with 2.952 (2) and 2.976 (2), 2.929 (3) Å in the respective YBCO structures.

Both of these changes were observed in $YBaMn_2O_5$ (Attfield *et al.*, 1996): there the Mn—O distances are 2.002 (2) and 2.004 (5), and Ba—O is 3.098 (5) Å. The Mn atom is 0.396 Å from the basal plane. It was not possible to model Co^{III},Cu^{II} ordering without further magnetic measurements, parallel to that proposed for Mn^{II},Mn^{III} in $YBaMn_2O_5$ on the basis of ferromagnetic ordering. The Y—O contact distance is similar to that in YBCO prepared under both high and low pressure (*e.g.* 2.405, 2.382 Å; Francois *et al.*, 1988).

Experimental

The crystal was grown by a modified flux method outlined in detail by Lin *et al.* (1991).

Crystal data

$YBa(Cu_{1.10}Co_{0.90})O_5$	Mo $K\alpha$ radiation
$M_r = 429.18$	$\lambda = 0.71069$ Å

Tetragonal
$P4/mmm$
$a = 3.8827\,(10)$ Å
$c = 7.546\,(2)$ Å
$V = 113.75\,(5)$ Å^3
$Z = 1$
$D_x = 6.265$ Mg m^{-3}
D_m not measured

Cell parameters from 22 reflections
$\theta = 21\text{–}50°$
$\mu = 29.4$ mm^{-1}
$T = 124\,(2)$ K
Irregular plate
0.30 × 0.20 × 0.01 mm
Lustrous black

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1984)
$T_{\min} = 0.066$, $T_{\max} = 0.779$
682 measured reflections
254 independent reflections

245 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0387$
$\theta_{\max} = 39.9°$
$h = -1 \rightarrow 7$
$k = -1 \rightarrow 7$
$l = -1 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.064$
$S = 1.316$
254 reflections
17 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.0088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 3.09$ e Å^{-3}
$\Delta\rho_{\min} = -3.08$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.061 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba	1/2	1/2	0	0.01124 (15)
Y	1/2	1/2	1/2	0.00696 (15)
Cu1†	0	0	0.73395 (12)	0.0134 (2)
Co1‡	0	0	0.73395 (12)	0.0134 (2)
O1	0	0	0	0.0132 (8)
O2	1/2	0	0.6871 (4)	0.0101 (4)

† Site occupancy = 0.55 (3). ‡ Site occupancy = 0.45 (3).

Table 2. *Selected geometric parameters (Å, °)*

Ba—O1	2.7455 (7)	Cu1—O2	1.9733 (7)
Ba—O2$^{\rm i}$	3.057 (2)	Cu1—O1$^{\rm ii}$	2.0075 (10)
Y—O2	2.4002 (16)		
O2$^{\rm iii}$—Cu1—O2	159.34 (17)	Cu1$^{\rm v}$—O1—Cu1$^{\rm vi}$	180.0
O2$^{\rm iv}$—Cu1—O2	88.16 (3)	Cu1$^{\rm vii}$—O2—Cu1	159.34 (17)
O2—Cu1—O1$^{\rm ii}$	100.33 (8)		

Symmetry codes: (i) $x, 1 + y, z - 1$; (ii) $x, y, 1 + z$; (iii) $x - 1, y, z$; (iv) $-y, x, z$; (v) $-x, -y, 1 - z$; (vi) $x, y, z - 1$; (vii) $1 + x, y, z$.

The composition of the mixed Cu,Co site was determined by refinement (Sheldrick, 1996) with common positional and displacement parameters and a total unit-cell content of 2 [Cu 1.10 (5), Co 0.90 (5)]. The final maximum difference peaks are less than 0.6 Å from the Ba atom and are expected to reflect errors introduced by the absorption correction and crystal quality. The ψ scan absorption method (Sheldrick, 1984) was used because the crystal shape, and its smallest dimension, precluded accurate measurement and boundary-edge definitions.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS* and *SHELXTL* (Sheldrick, 1984). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *STRUPLO* (Fischer *et al.*, 1990). Software used to prepare material for publication: *SHELXL*96 *CIFTAB*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1169). Services for accessing these data are described at the back of the journal.

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The First Cadmium Rare Earth Borates $CdLn[B_5O_{10}]$ with Ln = La, Sm, Eu

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Abstract

Single crystals of the new compounds $CdLn[B_5O_{10}]$ (Ln = La^{3+}, Sm^{3+}, Eu^{3+}) were obtained in silver ampoules at 1073 K by using a B_2O_3 flux technique.