Tetragonal SmBa$_2$Cu$_3$O$_{7-x}$ [x = 0.74 (4)]

Shoichi Sato,[a]*† **Yoshihiro Kino,**[a] **Atsushi Shibata,**[a] **Masaru Nakamura,**[b]‡ **Christian Krauns**[b] **and Yuh Shiohara**[b]

[a]X-Ray Research Laboratory, Rigaku Corporation, 3-12-7 Matsubaracho, Akishima, Tokyo 196-8666, Japan, and [b]Superconductivity Research Laboratory, International Superconductivity Technology Centre, 10-13 Shinonome 1-chome, Koto-ku, Tokyo 135-0062, Japan

Correspondence e-mail: ss310@f2.dion.ne.jp

Crystals of the title compound, samarium barium copper oxide, were prepared by a modified top-seeded solution-growth method. The crystals thus prepared showed no superconductivity down to 4.2 K. A careful examination showed that the structure closely resembles that of tetragonal YBCO, and there is no atom mixing at the Ba or other sites, within experimental accuracy. A bond-valence-sum calculation at the Ba site also indicated the absence of Sm. Each site is fully occupied by a single atom, except for the oxygen site in the basal plane of the CuO$_6$ octahedron. The occupancy of this oxygen site is significantly reduced [0.13 (2)], as is commonly observed in the 123 system. The atomic displacement parameters of the atoms in the CuO$_2$ plane, as well as of the Sm atom, are very small, indicating that two equivalent CuO$_2$ planes tightly sandwich the Sm atom.

Comment

Since the high-temperature superconductivity of the Ba–La–Cu–O ceramic system was discovered by Bednorz & Müller (1986), several new compounds have been synthesized as high-T_c superconductors, of which YBa$_2$Cu$_3$O$_{7-x}$, also known as YBCO or a 123 compound, has been widely studied by many researchers after Wu *et al.* (1987). The title compound, (I), was prepared in the course of our studies into the super-conductivity of YBCO and its analogues. The possibility of the existence of a similar but non-stoichiometric compound was proposed by Yoo *et al.* (1994), in which excess Sm atoms occupy some of the Ba sites, so as to give the formula Sm$_{1+y}$Ba$_{2-y}$Cu$_3$O$_{7-x}$. Therefore, the X-ray structure analysis of (I) was carried out carefully in order to examine whether such atom mixing occurred or not, and also to determine the concentration of oxygen in the crystal. As-grown crystals showed no superconductivity down to 4.2 K. Of these, a crystal

† Current address: Kuboyamacho 1-9-109, Hachioji, Tokyo 192-0023, Japan.
‡ Current address: Laboratory, Mitsubishi Cable, 4-3 Ikejiri, Itami, Hyogo 664-0027, Japan.

was selected for the structure analysis. As shown below, the occupational disorder of the Sm atom at the Ba site was safely rejected, contrary to the disorder reported by Yoo *et al.* (1994). The oxygen content at the basal plane of the CuO$_6$ octahedron is very much reduced, so that the chemical formula can be written with a good degree of accuracy as SmBa$_2$Cu$_3$O$_{6.26}$.

Bond valence (Brown, 1992) is a sensitive test of the co-existence of Sm at the Ba site. The bond-valence sum at Ba (1.91, based on the observed Ba—O bond length) is close to, but slightly lower than, the valence of the Ba ion (2.0). If the Ba site were totally occupied by Sm without any other change of geometry, the bond-valence sum would be much less (1.12) than the expected value of 3.0 for the Sm ion. Therefore, if Sm were partially present on this site, the bond-valence sum would be even less than 1.91, not greater than the value expected from the true existence of the Sm ion. These calculations therefore indicate the absence of Sm at the Ba site.

The bond-valence sums at Cu2 and O3 are a little large (2.07 and 2.11, respectively), suggesting some slight compression of the CuO$_2$ plane. Conversely, the sums at Ba and O1 are a little low (1.91 and 1.89, respectively), suggesting that the BaO1 layer is stretched. These characteristics of the layers are in agreement with their atomic displacement parameters.

Fig. 1 illustrates the structure of (I). The cell dimensions show slight elongation from those of YBCO along both the *a* and *c* axes, reflecting the differences in ionic radii between Sm and Y ions. The Ba atom possesses almost isotropic vibration.
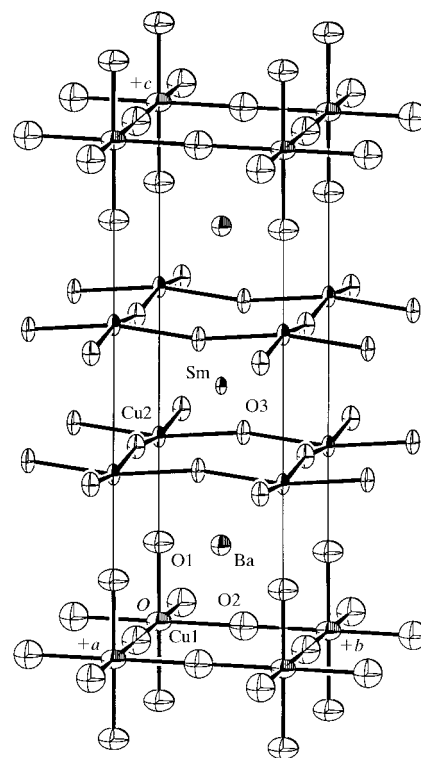

Figure 1
An *ORTEP*II (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are plotted at the 99% probability level. The very small U_{11} value of Cu2 caused an error in the plot; therefore, the ellipsoid of this atom has been magnified by 15%.

inorganic compounds

The U_{11} and U_{22} values of the Sm and Cu2 atoms, and U_{22} of the O3 atom, are very small, suggesting tight bonding in the sandwich formation. In the sandwich block, the O3$\cdots$O3 distance between the CuO$_2$ planes is shorter than that of Cu2$\cdots$Cu2. Thus, Cu2 deviates by 0.206 (2) Å from the square coordination plane of the O atoms towards O1. The deformed CuO$_2$ plane can also be seen from the O—Cu—O angles in Table 1.

Fig. 1 shows the anisotropic displacement ellipsoids for the Sm, Cu2 and O3 atoms. Although the ellipsoids themselves are not particularly large, the anisotropy indicates that these atoms vibrate more freely along the c axis, which is the direction perpendicular to the two-dimensional Cu2—O3 network, and that the bonding in the sandwich block might be relatively loose along the c axis. In contrast, the ellipsoids of atoms Cu1 and O1 of the octahedron are restrained along **c**, and this is probably correlated with the extremely short Cu1—O1 bond [1.810 (4) Å, which is about 0.03 Å shorter than the value reported for YBCO crystals]. Such modes of vibration are physically reasonable.

The much reduced occupancy of the O2 site suggests that the atom is loosely bound to the Cu1 and Ba atoms, so that it can be easily removed. An additional examination of one of the crystals grown under low oxygen pressure (1 kPa) was performed in a similar manner, and nearly the same result was obtained. In this instance, however, the occupancy of the O2 site was so much reduced as to be almost vacant. The low-oxygen crystals became superconducting (T_c = 93 K) after annealing in an oxygen atmosphere (Nakamura *et al.*, 1995).

Experimental

Crystals of (I) were prepared by a modified top-seeded solution-growth method in air. Details of the crystal growth and properties of the compound were reported by Nakamura *et al.* (1995).

Crystal data

$SmBa_2Cu_3O_{6.26}$	Mo $K\alpha$ radiation
$M_r = 715.85$	Cell parameters from 25
Tetragonal, $P4/mmm$	reflections
$a = 3.878$ (1) Å	$\theta = 26.1$–$28.5°$
$c = 11.818$ (2) Å	$\mu = 27.830$ mm^{-1}
$V = 177.76$ (6) Å^3	$T = 297.2$ K
$Z = 1$	Plate, black
$D_x = 6.69$ Mg m^{-3}	$0.50 \times 0.33 \times 0.12$ mm

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.030$
$\omega/2\theta$ scans	$\theta_{max} = 50.18°$
Absorption correction: analytical	$h = 0 \rightarrow 8$
(de Meulenaer & Tompa, 1965)	$k = 0 \rightarrow 8$
$T_{min} = 0.006$, $T_{max} = 0.122$	$l = 0 \rightarrow 25$
1148 measured reflections	4 standard reflections
641 independent reflections	every 150 reflections
533 reflections with $F^2 > 2\sigma(F^2)$	intensity decay: 0.35%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.019$	$\Delta\rho_{max} = 2.83$ e Å^{-3}
$wR = 0.026$	$\Delta\rho_{min} = -1.93$ e Å^{-3}
$S = 1.594$	Extinction correction: type 2 Gaus-
533 reflections	sian isotropic (Zachariasen, 1967)
21 parameters	Extinction coefficient: 1.59 (7)
$w = 1/[\sigma^2(F_o) + 0.00006|F_o|^2]$	

Table 1
Selected geometric parameters (Å, °).

Sm—O3	2.448 (1)	Cu1—O1	1.810 (4)
Ba—O1	2.7815 (7)	Cu1—O2	1.9391 (5)
Ba—O2	2.9892 (4)	Cu2—O1	2.398 (4)
Ba—O3	2.888 (2)	Cu2—O3	1.9501 (2)
O1—Cu2—O3	96.07 (7)	O3—Cu2—O3^{ii}	167.9 (1)
O3—Cu2—O3^{i}	89.36 (1)		

Symmetry codes: (i) $-y, x, z$; (ii) $x, y - 1, z$.

The observed reflections were averaged to a unique data set after the absorption correction. This averaging helps to reduce some of the error arising from shape effects in the correction. The absorption corrections were made carefully now outlined. The software package used includes analytical (de Meulenaer & Tompa, 1965) and numerical (Coppens *et al.*, 1965) correction methods for polyhedral crystals. In the present work, both methods gave nearly the same correction factors: T_{min}, T_{max} and T_{av} for the analytical method, with the corresponding values for the numerical method in brackets, were 0.006 (0.002), 0.122 (0.121) and 0.055 (0.054), respectively. A trial refinement after the analytical correction, however, converged to a lower R value (0.047) than for the numerical method (0.052). Therefore, the analytical correction was adopted. Next, *DIFABS* (Walker & Stuart, 1983) was applied to reduce the shape effect, before averaging. Prior to the application of *DIFABS*, weak reflections with intensities less than $5\sigma_o(I)$ were excluded from the reference refinement so as to eliminate the wrong influence on the correction. The refined parameters before and after the application of *DIFABS* did not show large differences, with values within one s.u. for the positional parameters and within three s.u.'s for the atomic displacement parameters. The occupancies of the Sm and Ba atoms were close to unity and coincided within one s.u. The largest difference was B_{iso} of atom O2; the value without *DIFABS* was very large (30), probably due to residual error in the intensity data. The structure was confirmed to be isomorphous with tetragonal YBCO by a check of the Patterson peaks. The initial coordinates of the structure were similar to those of a YBCO crystal (Sato *et al.*, 1988, 1989). A refinement of the occupancies of the Sm and Ba sites at a later stage resulted in 1.005 (3) for Sm and 1.006 (4) for Ba. The occupancies of other sites are also close to unity, with discrepancies of less than 1%, except for the O2 site, which showed large atomic deficiency, similar to other common 123 compounds. Thus, the site occupancy of the O2 atom was included in the final refinement with an isotropic atomic displacement parameter. Other atoms were fixed to unit occupancy. The possibility of Mg contamination in any of the cation sites owing to the use of an MgO seed crystal was also rejected.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku Corporation, 1998); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1311). Services for accessing these data are described at the back of the journal.

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