Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The superconductor $(\mathrm{Tl,Hg,Ca})_2(\mathrm{Ba,Sr})_2(\mathrm{Ca,Sr,Tl})\mathrm{Cu}_2\mathrm{O}_{7.6}$

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Received 18 June 2002
Accepted 22 July 2002
Online 21 August 2002

In the title 2212-type superconductor (thallium mercury calcium barium strontium copper oxide), which contains both Tl and Hg in the charge reservoir (CR), Sr is located at both alkali-earth (AE) metal sites. Ca enters the CR at the same time as Tl shares the smaller AE site, which increases the apical Cu—Cu distance significantly. The structure causes the superconducting Cu–O layers to become significantly puckered.

Comment

Ever since the 2212-type superconductors were discovered, originating from $\mathrm{Tl_2Ba_2CaCu_2O_8}$, which is as abbreviated 2212 (Subramanian *et al.*, 1988), several closely related compounds have been prepared, differing in their chemical substitutions. Hg was tried at the Tl site (Bryntse, 1994) and Sr was introduced at both the Ba and the Ca site in different amounts (Maignan *et al.*, 1995; Valldor *et al.*, 2000). Single crystals of $(\mathrm{Tl,Hg})_2\mathrm{Sr_2CaCu_2O}_{8-d}$ were obtained using a high-pressure–high-temperature technique (Valldor *et al.*, 1999). The starting composition $\mathrm{Tl_{1.3}Hg_{0.7}BaSr_{1.5}Ca_{0.5}Cu_2O}_{8-d}$ was also tried for a single-crystal growth and this structural study will be presented below. To ensure that the crystal analysed was representative of the whole sample, unit-cell parameters were also calculated from powder diffraction data using a Guinier–Hägg camera on ground single crystals [$a = 3.8353$ (5) Å and $c = 29.138$ (6) Å]. The unit-cell parameters obtained from the single-crystal diffractometer data were $a = 3.8380$ (6) Å and $c = 29.145$ (7) Å. Ten elemental analyses (EDS, *i.e.* energy dispersive spectroscopy) were performed on the single crystal after diffraction data had been collected and the resulting stoichiometry [$\mathrm{Tl_{1.22(4)}Hg_{0.79(4)}Ba_{0.86(3)}Sr_{1.48(4)}Ca_{0.63(2)}Cu_{2.03(6)}O}_x$] agreed with the starting composition ($\mathrm{Tl_{1.3}Hg_{0.7}BaSr_{1.5}Ca_{0.5}Cu_2O}_x$). The only significant difference was the lower Ba content in the product balanced by a higher Ca content.

The results from EDS were used to generate the occupancies at the different sites in the structure, as illustrated in Fig. 1. The starting point of the fractional coordinates for all atoms was taken from the work of Subramanian *et al.* (1988). The reason for atoms O2 and O3 only being refined isotropically was the limited number of observed reflections with an intensity/background ratio greater than 3. The first model obtained, with only (Tl,Hg) in the charge reservoir (CR) and (Ca,Sr) at the smaller alkali-earth (AE1) metal site between the Cu–O layers, resulted in unfavourable atomic displacement parameters at both sites, *i.e.* a large U value for (Tl,Hg) and a negative U value for (Ca,Sr). Both Tl and Hg were earlier observed at the AE1 site in a high-pressure synthesized 2212-type phase (Wu *et al.*, 1998), however, Wu *et al.* reported this as a new stacking order. The CR on the other hand was occupied by both Ca and Cu in another superconducting material, also formed under high-pressure conditions (Chu *et al.*, 1997). Since our crystal was synthesized under pressure as well, Ca was introduced at the CR site at the same time as a minor amount of Tl was placed at the AE1 site. When refining the occupancies, all sites were assumed fully occupied, except for the O3 site, which ended up as 78 (5)% occupied after refinement. Ba, Hg, Cu and O were all placed at their presumed sites, while Sr was placed at both AE sites with fixed values taken from EDS results. Tl and Ca were placed in the CR and at the AE1 site. The total amounts of each of the two metals were kept constant, according to EDS results, and only their relative occupations at both sites were refined, using one parameter. The metal distribution according to the refinement was $(\mathrm{Tl_{0.582(2)}Hg_{0.395}Ca_{0.023(2)}})_2(\mathrm{Ba_{0.435}Sr_{0.565}})_2(\mathrm{Sr_{0.36}Ca_{0.594(5)}Tl_{0.046(5)}})\mathrm{Cu_2}$. This resulted in both atomic displacement parameters ending up positive and reasonable.

In the final model, only atom O3 had a large atomic displacement. However, in many papers, this O atom is displaced from the high-symmetry position $(0, 0, z)$ to (x, x, z) (see, for example, Subramanian *et al.*, 1988), which could be a reason for this relatively high value. Calculated bond lengths and angles are reasonable (Table 1). The CR metal atoms (Tl,Hg,Ca) are situated in distorted octahedra, with shorter apical distances that suit the Hg^{2+} atom (40%), for which linear coordination is common.

From bond lengths between Cu and O, the bond-valence sum of Cu is calculated as BVS(Cu) = 2.195 (9). Assuming nominal oxidation states for all metal atoms, the calculated oxygen content would be 7.62, which agrees well with the refined value of 7.6 (2). The measured crystal was too small for resistivity of susceptibility measurements, however, if the BVS of Cu is the main property connected to T_c in this system, the BVS–T_c comparison (Valldor *et al.*, 2000) could be used to conclude that T_c should be within the range 75–90 K. From the same report, it is possible to conclude that both cell parameters and EDS analyses agree well with a T_c of about 80 K. When comparing the interatomic distances in $\mathrm{Tl_2Ba_2CaCu_2O_8}$ (Table 2; **B**, Subramanian *et al.*, 1988) with those presented here (Table 2, **A**), several things are made clear. The CR in **A** is larger than that in **B**, which also could be an indication of a minor Ca content at this site in **A**, since Ca^{2+} has a larger ionic radius compared with both Tl^{3+} and Hg^{2+}. The larger AE site (AE2) has shorter metal-to-oxygen bonds in **A**, as expected,

DOI: 10.1107/S0108270102013148

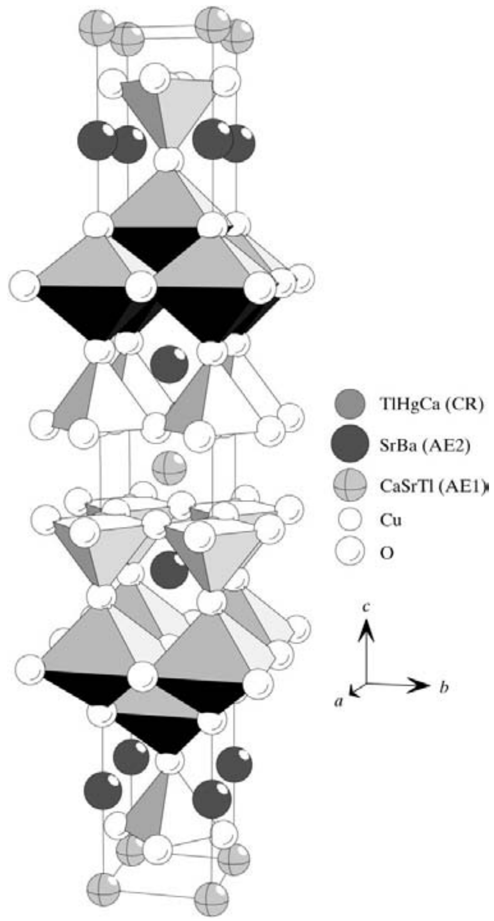

Figure 1
The 2212 structure explaining the elemental distribution.

since the site is partially occupied by Sr. An important observation is the size difference of the AE1 site, where **A** has longer metal-to-oxygen bonds, also due to the presence of Sr. When comparing the O—Cu—O angles, it is obvious that **A** is more puckered than **B**. The puckering of the Cu–O layers and the presence of Sr at the AE1 site cause the apical Cu—Cu distance across the AE1 layer to be almost 0.2 Å longer in **A** than in **B**. A difference Fourier analysis was carried out and the maxima of 1.39 and −2.74 e Å^{-3} were both found close to the AE2 site. The maxima are tolerable considering the high electron densities already present at the AE2 site. This high-pressure synthesis study agrees with previous reports concerning mixed sites (Chu *et al.*, 1997; Wu *et al.*, 1998), *i.e.* Cu as well as Ca enter the CR and Tl can be found at the AE1 site.

Experimental

In order to obtain high purity starting materials, Tl_2O_3, HgO and CuO were heated at 420 K overnight to remove moisture, while $CaCO_3$ was decomposed into CaO at 1270 K over a period of 20 h. SrO and BaO were prepared by heating their carbonates at 1320 K under dynamic vacuum (<6.0 × 10^{-6} mbar; 1 mbar = 100 Pa) and the oxides formed were subsequently transported to a glove-box. All the metal oxides were weighted, mixed in an agate mortar, and formed into pellets under inert conditions inside the glove-box. The metal-to-metal ratios were chosen to reach the nominal composition $Tl_{1.3}Hg_{0.7}BaSr_{1.5}Ca_{0.5}Cu_2O_{8-d}$, with the aim of placing Sr at two crystallographic sites in the 2212 structure. The pellets were placed in a $BaZrO_3$ crucible and placed inside a high-pressure chamber, which is described in detail by Morawski *et al.* (1997). Ar pressure (0.9 GPa) was applied before the heat treatment began. The reaction progressed in several steps: the pre-reaction heating (1190 K, 1 h), the melting (1410 K, 2 min), and the crystal growth (−24 K h^{-1} to 1230 K), after which the heating was discontinued and the sample allowed to cool to room temperature. The crystals, found inside the crucible after the reaction, were all black, opaque and plate-like. Elemental analyses (EDS) of the crystals were performed inside a scanning electron microscope (Jeol SEM 820) attached with a LINK AN10000 system. When refining the unit-cell parameters, X-ray powder diffraction analysis was performed using elemental Si as the internal standard in a Guinier–Hägg focusing camera (Cu $K\alpha_1$, λ = 1.5405 Å).

Crystal data

$(Tl,Hg,Ca)_2(Ba,Sr)_2(Ca,Sr,Tl)$-$Cu_2O_{7.6}$
M_r = 930.2
Tetragonal, $I4/mmm$
a = 3.8380 (6) Å
c = 29.145 (7) Å
V = 429.3 (1) Å^3
Z = 2
D_x = 7.194 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 121 reflections
θ = 2.8–23.9°
μ = 55.06 mm^{-1}
T = 293 (2) K
Plate, black
0.10 × 0.05 × 0.01 mm

Data collection

Stoe IPDS diffractometer
Area-detector scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
$T_{\min}$ = 0.057, $T_{\max}$ = 0.210
1228 measured reflections
138 independent reflections

121 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.046
$\theta_{\max}$ = 23.9°
$h = -4 \rightarrow 4$
$k = -4 \rightarrow 4$
$l = -32 \rightarrow 31$

Refinement

Refinement on F
R = 0.020
wR = 0.021
S = 2.41
138 reflections

22 parameters
$w = 1/[\sigma^2(F) + 0.000036F^2]$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.39 e Å^{-3}
$\Delta\rho_{\min}$ = −2.74 e Å^{-3}

Table 1
Selected interatomic distances (Å).

Tl—O2	2.01 (1)	Ba—O3	2.79 (2)
Tl—O3	2.7183 (9)	Sr2—O1$^{\rm ii}$	2.514 (4)
Tl—O3$^{\rm i}$	2.02 (2)	Cu—O1	1.9199 (2)
Ba—O1$^{\rm ii}$	2.729 (5)	Cu—O2	2.50 (1)
Ba—O2$^{\rm iii}$	2.784 (2)		

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $x, y-1, z$; (iii) $x-1, y-1, z$.

Table 2
Interatomic distances (Å) and angles (°) in the title 2212 structure (**A**) compared with $Tl_2Ba_2CaCu_2O_8$ (**B**; Subramanian *et al.*, 1988).

Parameter in **A**	Value in **A**	Number	Value in **B**	Parameter in **B**
(Tl,Hg,Ca)—O2	2.01 (1)	1	1.979 (9)	Tl—O2
(Tl,Hg,Ca)—O3	2.02 (2)	1	1.99 (2)	Tl—O3
(Tl,Hg,Ca)—O3	2.718 (1)	4	2.46 (2)	Tl—O3
(Sr,Ba)—O3	2.79 (2)	1	2.86 (2)	Ba—O3
(Sr,Ba)—O2	2.784 (2)	4	2.818 (2)	Ba—O2
(Sr,Ba)—O1	2.729 (5)	4	2.788 (4)	Ba—O1
(Ca,Sr,Tl)—O1	2.514 (4)	8	2.478 (4)	Ca—O1
Cu—O2	2.50 (1)	1	2.700 (9)	Cu—O2
Cu—O1	1.9199 (2)	4	1.928 (0)	Cu—O1
Cu—Cu	3.366 (2)	1	3.166 (4)	Cu—Cu(apical)
O1—Cu—O1	176.7 (4)	2	178.43 (0)	O1—Cu—O1
O1—Cu—O2	91.7 (2)	4	90.78 (9)	O1—Cu—O2

The reflection-to-parameter ratio was low at 6.3 (138/22). This problem was not discovered until the crystal had been covered with gold for elemental analyses. The goodness-of-fit is slightly too high, which might be due to the problem with correctly weighting the weak reflections against the strong.

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1996) and *X-SHAPE* (Stoe & Cie, 1996); program(s) used to solve structure: *JANA*98 (Petricek & Dusek, 1997); program(s) used to refine structure: *JANA*98; molecular graphics: *DIAMOND* (Brandenburg, 2001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1382). Services for accessing these data are described at the back of the journal.

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