

LETTERS TO THE EDITOR

Crystal Structure of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$

M. A. SUBRAMANIAN, J. B. PARISE, J. C. CALABRESE,
C. C. TORARDI, J. GOPALAKRISHNAN, AND A. W. SLEIGHT

*Central Research and Development Department, E. I. Du Pont de Nemours
and Company, Experimental Station, Wilmington, Delaware 19898*

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Crystals of the 110 K superconductor $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ have been grown and the structure refined from single-crystal X-ray diffraction data: $a = 3.853(1)$, $c = 15.913(4)$ Å, space group $P4/mmm$, $R = 0.055$, $R_w = 0.057$. The structure contains triple copper-oxygen sheets separated by Ca ions which show ~5% Tl substitution. These units alternate with single Tl-O layers. The existence of correlated atomic displacements within the thallium-oxygen sheets is again suggested by a disordered Tl-O arrangement in the average structure. The triple Cu-O sheets in $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ are stacked directly above each other, whereas in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, which contains double Tl-O sheets, alternate units are shifted by $(a_1 + a_2)/2$. © 1988 Academic Press, Inc.

Introduction

The discovery of superconductivity in the Tl-Ba-Ca-Cu-O system (1) has led to the identification of a new homologous series of superconducting copper-containing oxides, $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, in which the transition temperature increases with the number (n) of Cu-O layers (2). The structures of the $n = 1, 2$, and 3 members of the series, determined by single-crystal X-ray and powder neutron diffraction methods (2-6), consist of rocksalt-like double Tl-O layers separating perovskite-like $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ slabs. Recent reports (7, 8) indicate that another series of superconducting oxides exists in the Tl-Ba-Ca-Cu-O system where a single Tl-O layer separates the perovskite-like copper oxide slabs. A preliminary structure of one of the compounds

in this family, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, was obtained by powder X-ray diffraction analysis (7). For the first time, single crystals of this phase have been grown; we report here on the preparation, single-crystal X-ray structure, and superconducting properties of these crystals.

Experimental

Single crystals of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ were grown from a copper-rich melt with oxides (Tl_2O_3 , BaO_2 , CaO_2 , and CuO) in the molar ratio 1 : 2 : 2 : 4 (Tl : Ba : Ca : Cu) in a sealed gold tube. The mixture was heated to 925°C, held for 6 hr, and cooled at 1°C/min. Plate-like crystals found in the melt were mechanically separated and used for further characterization and structure determination. Magnetic flux exclusion measure-

TABLE I
SUMMARY OF CRYSTALLOGRAPHIC INFORMATION
FOR $Tl_{1.1}Ba_{1.9}Ca_{1.9}Cu_3O_9$

Dimensions (mm)	0.13 × 0.16 × 0.004
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo $K\alpha$
Monochromator	Graphite
Formula weight	897.1
Crystal system	Tetragonal
Space group	$P4/mmm$ (No. 123)
Cell constants (Å)	$a = 3.853(1)$ $c = 15.913(4)$
Temperature	Ambient
Calc. density (g cm ⁻³)	6.30 ($Z = 1$)
Scan mode	ω
2 θ range (°)	0–60
Octants	+++ , -++ , --+ , +++
μ (cm ⁻¹)	346.4
Absorption correction	Analytical
Transmission factors	0.043–0.777
Total reflections	1417
Independent reflections	223 ($I > 3\sigma$)
Data/parameters	9.3
R	0.055
R_w	0.057

ments on the crystals revealed a sharp T_c onset of ~ 110 K as reported earlier (7).

Single-crystal X-ray diffraction information for $TlBa_2Ca_2Cu_3O_9$ is summarized in Table I. Neither long exposure Weissenberg photographs nor diffractometry scans in the [100], [010], or [001] directions indicated the presence of satellite peaks similar to those found in $Bi_2Sr_2CaCu_2O_8$ (9). The data were reduced to structure factors, corrected for absorption, and averaged in $P4/mmm$ symmetry. Atomic positions were taken from the structure proposed for this material (7). The structural model was refined by full-matrix least-squares analysis using neutral atom scattering factor curves with anomalous scattering terms and anisotropic thermal motion for the metal atoms. Occupation factors were refined for the metal atoms and found to be low for Ba and high for Ca, indicating the presence of vacancies in the Ba site and substitution of $\sim 5\%$ Tl for Ca, similar to the situation found in $Tl_2Ba_2CaCu_2O_8$ (3) and in $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2). In contrast to the latter two

materials, the thallium sheets in $TlBa_2Ca_2Cu_3O_9$ are fully occupied. Thus, the formula obtained from the refinement is $Tl_{1.1}Ba_{1.9}Ca_{1.9}Cu_3O_9$. Large thermal motion was observed for the thallium atoms, $B = 4.9 \text{ \AA}^2$, and oxygen atoms, O(4), within the thallium sheets, $B = 2.6 \text{ \AA}^2$, as previously seen in the structures of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1, 2, \text{ and } 3$) (2–5). The highly anisotropic motion of the Tl atoms, $B_{11} = 7.2(2)$ and $B_{33} = 0.4(1) \text{ \AA}^2$, when placed at 0,0,0, suggests that the Tl atoms are actually displaced from this ideal position. A significant improvement in the R factors was obtained when this atom was refined in the 4l sites ($x, 0, 0$) giving a statistically disordered four-fold positioning around 0,0,0. However, shifting oxygen atom O(4) from its ideal site did not improve the discrepancy factors. Positional and thermal parameters are given in Tables II and III. Interatomic distances and angles are listed in Table IV.

TABLE II
POSITIONAL^a AND THERMAL^b PARAMETERS FOR THE
ATOMS OF $Tl_{1.1}Ba_{1.9}Ca_{1.9}Cu_3O_9$

Atom	Site	x	y	z	B (Å ²)
Tl(1) ^c	4l	0.085(2)	0.00	0.00	1.7(1)'
Ba(1) ^d	2h	0.50	0.50	0.1729(1)	0.6(1)'
Cu(1)	1b	0.00	0.00	0.50	0.4(1)'
Cu(2)	2g	0.00	0.00	0.2991(2)	0.4(1)'
Ca(1) ^e	2h	0.50	0.50	0.3953(3)	0.7(1)'
O(1)	2e	0.00	0.50	0.50	0.9(3)
O(2)	4i	0.00	0.50	0.3019(7)	1.1(2)
O(3)	2g	0.00	0.00	0.1277(11)	0.6(3)
O(4) ^f	1c	0.50	0.50	0.00	2.6(7)

^a Space group $P4/mmm$ (No. 123).

^b All metal atoms refined with anisotropic thermal parameters; equivalent isotropic thermal parameter is listed.

^c Refined off of the ideal site. The Tl site was found to be completely filled with thallium.

^d Occupancy factor refined to 0.94(1) atom/site.

^e Site composition fixed at 0.95 Ca + 0.05 Tl.

^f Refining this atom off of the ideal site did not improve the discrepancy factors.

TABLE III
ANISOTROPIC THERMAL PARAMETERS^a (Å²)
FOR THE METAL ATOMS OF
Tl_{1.1}Ba_{1.9}Ca_{1.9}Cu₃O₉

Atom	B_{11}	B_{22}	B_{33}
Tl(1)	3.2(4)	1.7(2)	0.36(6)
Ba(1)	0.44(5)	0.44	0.99(6)
Cu(1)	0.4(1)	0.4	0.4(1)
Cu(2)	0.3(1)	0.3	0.6(1)
Ca(1)	0.4(1)	0.4	1.2(1)

^a $\exp[-0.25(B_{11}h^2a^*2 + 2(B_{12}hka^*b^* + \dots))]$; $B_{12} = B_{13} = B_{23} = 0.0$.

Results and Discussion

Figure 1 compares the crystal structures of TlBa₂Ca₂Cu₃O₉ and Tl₂Ba₂Ca₂Cu₃O₁₀. Both structures contain triple sheets of corner-shared CuO₄ groups which are oriented

parallel to the (001) plane. Additional oxygen atoms are located above and below the triple Cu-O sheets and are positioned at a distance of 2.7 Å from the copper atoms. As in Tl₂Ba₂Ca_{n-1}Cu_nO_{2n+4} ($n = 2$ and 3), there are no oxygen atoms between adjacent Cu-O sheets. The individual Cu-O sheets are separated by 3.2 Å (Cu-Cu distance), with Ca (and some Tl) ions coordinated to eight oxygen atoms. Barium ions reside just above and below the Cu-O triple sheets in ninefold coordination with oxygen. The Ba-Cu-Ca-Cu-Ca-Cu-Ba slabs in TlBa₂Ca₂Cu₃O₉ alternate with a single Tl-O layer, whereas in Tl₂Ba₂Ca₂Cu₃O₁₀, these slabs alternate with double Tl-O sheets. Thallium bonds to six oxygen atoms in a distorted octahedral arrangement where the octahedra share edges within the sheet. In TlBa₂Ca₂Cu₃O₉, with Tl disordered on the 4l sites, two short and two

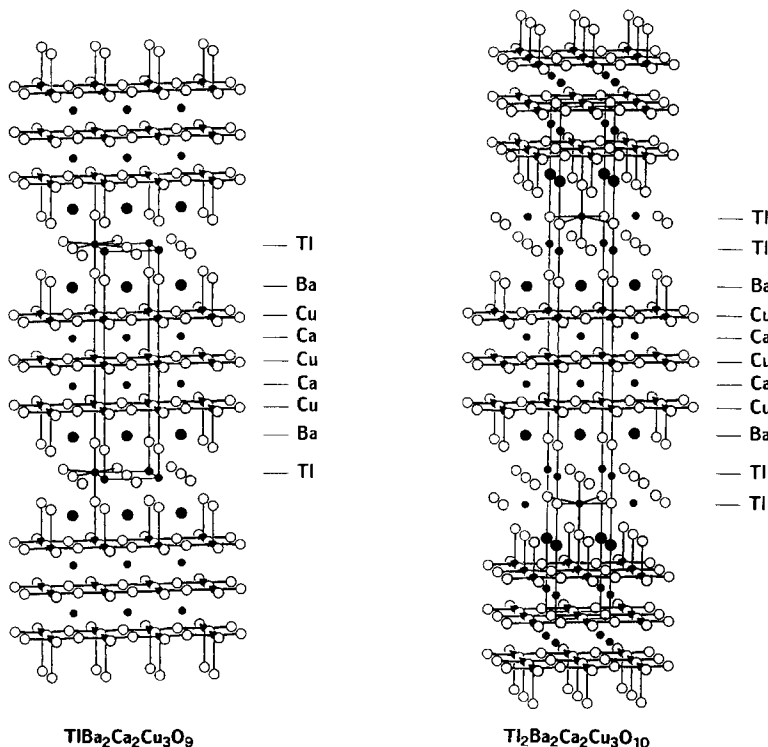


FIG. 1. A comparison of the structures of TlBa₂Ca₂Cu₃O₉ and Tl₂Ba₂Ca₂Cu₃O₁₀.

TABLE IV
INTERATOMIC DISTANCES (Å) AND ANGLES
(deg) IN $Tl_{1.1}Ba_{1.9}Ca_{1.9}Cu_3O_9$

Cu(1)–O(1)	1.9265(5)	(×4)
Cu(2)–O(2)	1.9270(6)	(×4)
Cu(2)–O(3)	2.73(2)	(×1)
Cu(1)–Cu(2)	3.198(3) (intersheet)	
Tl(1)–O(3)	2.06(2)	(×2)
Tl(1)–O(4)	2.503(4)	(×2)
Tl(1)–O(4)	2.966(5)	(×2)
Ba(1)–O(2)	2.816(9)	(×4)
Ba(1)–O(3)	2.818(4)	(×4)
Ba(1)–O(4)	2.751(2)	(×1)
Ca(1)–O(1)	2.547(2)	(×4)
Ca(1)–O(2)	2.433(8)	(×4)
O(1)–Cu(1)–O(1)	180.0	(×2)
O(1)–Cu(1)–O(1)	90.0	(×4)
Cu(1)–O(1)–Cu(1)	180.0	(×1)
O(2)–Cu(2)–O(2)	177.3(8)	(×2)
O(2)–Cu(2)–O(2)	89.97(2)	(×4)
O(2)–Cu(2)–O(3)	91.3(4)	(×4)
Cu(2)–O(2)–Cu(2)	177.3(8)	(×1)

long bonds result in the plane of the Tl atoms, of length 2.50 and 2.97 Å (Table IV). These distances compare well with the analogous Tl–O distances in $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1, 2, 3$) where the intrasheet oxygen atoms are displaced from their ideal site resulting in local chains or pairs (2, 10). In the case of $TlBa_2Ca_2Cu_3O_9$, the triple copper oxygen sheet units are stacked exactly one above the other (Fig. 1) whereas in $Tl_2Ba_2Ca_2Cu_3O_{10}$, the units are shifted by $(a_1 + a_2)/2$; this is clearly reflected in the approximate doubling of the c lattice dimension for the latter compound.

The oxidation states could be represented as $Tl^{III}Ba_2^{II}Ca_{n-1}^{II}Cu_n^{II}O_{2n+4}$ for the double Tl–O layer series, whereas this representation becomes $Tl^{III}Ba_2^{II}Ca_{n-1}^{II}Cu^{III}Cu_n^{II}O_{2n+3}$ for the single Tl–O layer series. This formulation implies a higher average copper oxidation state for the Tl–O single layer series, which in turn might lead to

higher T_c 's. Higher T_c 's are, however, not observed for the Tl–O single-layer series, which suggests that the copper oxidation state is more directly related to nonstoichiometry and overlap of the Tl 6s band with the Fermi level.

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