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Synthesis and Characterization of Orthorhombic $TlSr_2CuO_5$

A. K. GANGULI AND M. A. SUBRAMANIAN

Central Research and Development, E. I. Dupont de Nemours & Co.,
Experimental Station, Wilmington, Delaware 19880-0262

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$TlSr_2CuO_5$ has been synthesized in polycrystalline form. Powder X-ray diffraction studies indicate an orthorhombic structure; space group *Pmmm*; $a = 3.661(2)$, $b = 3.793(1)$, $c = 8.99(3)$ Å. The presence of short Cu–O bonds indicates the high formal valence for Cu. $TlSr_2CuO_5$ is found to be metallic and no superconductivity could be observed down to 4.2 K. © 1991 Academic Press, Inc.

Introduction

Thallium-containing superconductors can be described by the general formula $Tl_mCa_{n-1}Ba_2Cu_nO_{2n+m+2}$, where $n = 1, 2, 3, 4$ and $m = 1, 2$ (m indicating the number of Tl–O layers and n indicating the number of Cu–O sheets) (*1*, *2*). All of these oxides are superconducting with transition temperatures of 80 to 125 K, except for the $m = 1$, $n = 1$ member $TlBa_2CuO_5$, which is semiconducting (*3*). Analogous Sr (in place of Ba)-containing superconductors of the type $Tl_mCa_{n-1}Sr_2Cu_nO_{2n+m+2}$ could not be synthesized as pure phases, although there are some reports pertaining to these oxides in the literature (*4*, *5*). However, these phases have been stabilized by various substitutions like Pb (*6–9*), Bi (*10–12*), rare earth metals (*13–15*), and transition metals like Fe and Co (*16*). Only single-layer thallium compounds ($m = 1$), could be synthesized in the Sr-containing family of cuprates. The highest T_c obtained among the Sr-containing cuprates is 122 K for $Tl_{0.5}Pb_{0.5}Ca_2Sr_2Cu_3O_9$ (*6*). Our continued efforts to synthesize $TlSr_2CuO_5$ (denoted by 121), the $n = 1$ member of the $TlCa_{n-1}Sr_2Cu_nO_{2n+3}$ series, have been successful; in this communication we report on the synthesis, structure, and properties of this novel oxide.

Experimental

$TlSr_2CuO_5$ was synthesized by heating a mixture of Tl_2O_3, SrO_2, and CuO in sealed gold tubes at 875°C for 24 hr. Powder X-ray diffraction data were obtained by using a Scintag PAD IV X-ray diffractometer with Cu *Kα* radiation. Unit cell parameters were refined using a least-squares fitting procedure. The presence of superconductivity was checked by the ac induction technique down to 4.2 K. Four-probe resistivity measurements were carried out on bar-shaped samples.

Results

A variety of synthetic conditions were employed to obtain the appropriate temperature and heating schedule required to syn-

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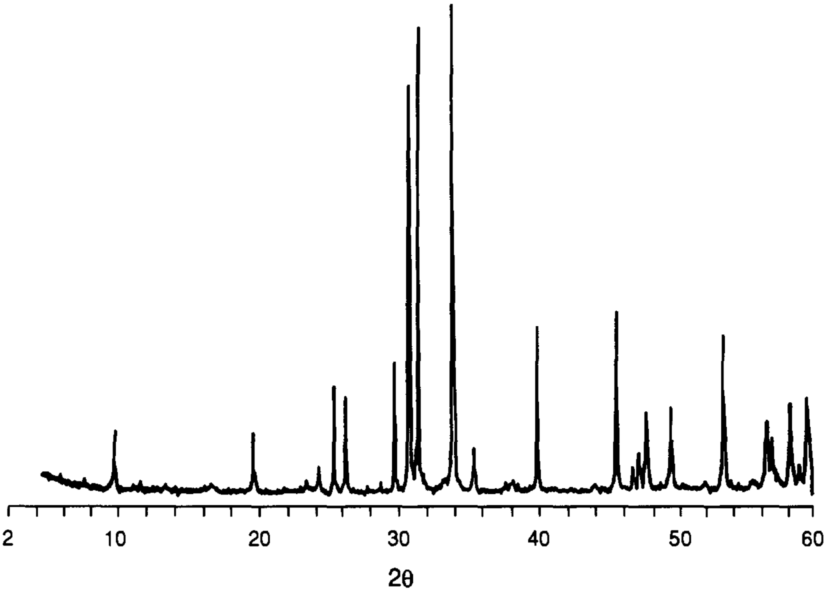

FIG. 1. Powder X-ray diffraction pattern of $TlCr_2SuO_5$.

thesize $TlSr_2CuO_5$. It was found that in most of the preparations, Sr_2CuO_3 formed as an impurity phase, along with $TlSr_2CuO_5$ as the major phase. We could essentially eliminate this parasitic phase by heating for long time periods (24 hr) at 875°C, although a few weak impurity lines (1–3%) still persisted. In Fig. 1 we show the X-ray powder diffraction pattern of $TlSr_2CuO_5$. The X-ray powder pattern could be indexed on an orthorhombic unit cell (space group: *Pmmm*) ignoring the weak impurity lines. The unit-cell parameters a = 3.661(2), b = 3.793(1), and c = 8.99(3) Å were obtained by a least-squares fit of the observed d-values. The observed intensities were compared with those calculated using LAZY-PULVERIX. The positional and thermal parameters (Table I) are approximate and have been guided by earlier refinements (*6, 16, 17*) of related Tl–Sr cuprates. In Table II we show the observed and calculated d-values and intensities. Although the positional and thermal parameters are approximate we find quite good agreement between observed and calculated intensities. In Table III we compare the bond lengths of $TlSr_2CuO_5$ (orthorhombic), obtained from our preliminary structural analysis, and those of other related 121 Tl cuprates. Magnetic measurements by the ac induction technique did not show any superconductivity down to 4.2 K. Four-

TABLE I

POSITIONAL AND THERMAL PARAMETERS[a] USED FOR CALCULATING INTENSITIES FOR $TlSr_2CuO_5$ (ORTHORHOMBIC)

Atom	x	y	z	B_{iso} (Å^2)
Tl	0	o	0	1.8
Sr	0.5	0.5	0.295	1.6
Cu	0	0	0.5	1.2
O(1)	0	0	0.2236	1.6
O(2)	0	0.5	0.5	1.2
O(3)	0.5	0.5	0	3.2
O(4)	0.5	0	0.5	1.2

[a] Positional and thermal parameters are approximate and have been guided by earlier refinements of related Tl cuprates (*6, 16, 17*).

TABLE II

CALCULATED AND OBSERVED INTENSITIES (AND *d*-VALUES) OBTAINED FOR $TlSr_2CuO_5$ USING LAZY-PULVERIX

h	*k*	*l*	*d*(obs)	*d*(cal)	I/I_o (obs)	I/I_o (cal)
0	0	1	9.002	8.990	12	17
	—		7.630	—	1	—
	—		6.621	—	1	—
	—		5.319	—	1	—
0	0	2	4.500	4.495	13	16
0	1	0	3.795	3.793	3	6
1	0	0	3.667	3.661	6	6
0	1	1	3.497	3.495	23	29
1	0	1	3.395	3.391	19	27
	—		3.099	—	3	—
0	0	3	2.998	2.997	28	18
0	1	2	2.900	2.899	86	83
1	0	2	2.839	2.839	92	78
1	1	0	2.635	2.634	100	100
1	1	1	2.530	2.528	9	15
	—		2.379	—	2	—
0	1	3	2.348	2.351	2	1
1	0	3	2.320	2.319	1	1
1	1	2	—	2.273	—	2
0	0	4	2.246	2.248	36	25
	—		2.046	—	1	—
1	1	3	1.978	1.978	37	34
0	1	4	1.934	1.934	5	7
1	0	4	1.916	1.915	7	7
0	2	0	1.898	1.897	16	22
0	2	1	1.858	1.856	2	1
2	0	0	1.829	1.831	18	19
0	0	5	—	1.798	—	<1
2	0	1	—	1.794	—	1
0	2	2	1.750	1.747	2	2
1	1	4	1.708	1.710	33	27
2	0	2	—	1.695	—	2
1	2	0	—	1.684	—	1
1	2	1	1.653	1.655	2	6
2	1	0	—	1.649	—	1
0	1	5	1.623	1.625	13	9
2	1	1		1.622		6
1	0	5	1.614	1.614	12	9
0	2	3	1.602	1.603	5	5
1	2	2	1.576	1.577	19	23
2	0	3	1.562	1.562	5	5
2	1	2	1.548	1.548	20	22

Note: The positional and thermal parameters used are given in Table I.

[a] Space Group: *Pmmm*. Unit cell parameters: $a = 3.661(2)$, $b = 3.793(1)$, and $c = 8.99(3)$ Å.

probe resistivity data show metallic behavior down to 77 K (Fig. 2).

Discussion

Earlier studies on the sythesis of oxides in the Tl–Sr–Cu–O system had difficulties in producing bulk single-phase oxides without the presence of suitable substitutions. It appears that under the conditions normally employed, phases like Sr_2CuO_3, $SrCuO_2$, and $TlSr_4O_7$ separate out as major phases. Synthesis of $TlSr_2CuO_5$ has the added disadvantage of stabilizing Cu in the trivalent state. Although $TlBa_2CuO_5$ (the Ba analog of $TlSr_2CuO_5$) has been reported to have been synthesized (*3*), bulk synthesis of $TlBa_2CuO_5$ has been difficult and further studies are necessary to obtain the appropriate synthetic conditions.

This report shows that bulk synthesis of $TlSr_2CuO_5$ is possible under appropriate conditions. The powder pattern (Fig. 1) could be indexed to the orthorhombic cell (Table II), barring a few weak lines having intensities of 1–3%. It is interesting to note that the structure is orthorhombic, while all other thallium cuprates so far discovered crystallize in the tetragonal *P4/mmm* (for single-layer Tl–O cuprates) or *I4/mmm* (for double-layer Tl–O cuprates) space groups. The only other exception is $Tl_2Ba_2CuO_6$, which crystallizes in both tetragonal or orthorhombic structures, the orthorhombic distortion being 0.03 Å (*18*). We have recently come across a preliminary report (*19*)

TABLE III

COMPARISON OF SELECTED INTERATOMIC DISTANCES (Å) OF ORTHORHOMBIC $TlSr_2CuO_5$ (THIS STUDY),[a] Tetragonal $TlSr_2CuO_5$ (*17*), $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ (*20*), AND $TlSr_2Cu_{0.4}Fe_{0.6}O_5$ (*16*)

Bond	$TlSr_2CuO_5$ (ortho)	$TlSr_2CuO_5$ (tetra)	$Tl_{0.5}Pb_{0.5}Sr_2CuO_5$	$TlSr_2Cu_{0.4}Fe_{0.6}O_5$
Cu–O(1)	2.485	2.489	2.491	2.324
Cu–O(2)	1.897	1.867	1.865	1.885
Cu–O(4)	1.831	—	—	—
Sr–O(1)	2.713	2.718	2.718	2.704
Sr–O(2)	2.597	2.626	2.619	2.653
Sr–O(3)	2.652	2.687	2.684	2.575
Sr–O(4)	2.644	—	—	—
Tl–O(1)	2.010	2.014	2.022	2.111
Tl–O(3)	2.635[b]	2.239–2.671	2.224–2.751	2.163–2.820

[a] Preliminary structural analysis using powder X-ray data.

[b] Disorder of Tl and O(3) atoms was not considered.

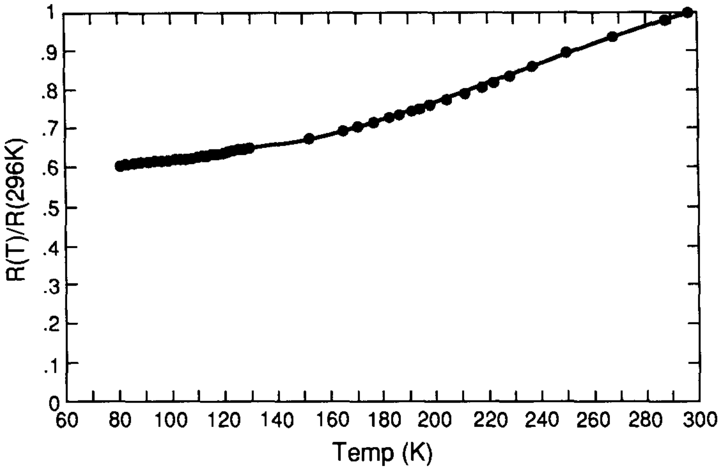

FIG. 2. Variation of the normalized resistance with temperature for $TlSr_2CuO_5$.

on an orthorhombic phase in the Tl–Sr–Cu–O system similar to what we find in this study.

An earlier report on $TlSr_2CuO_5$ by the single-crystal X-ray method (*17*) finds it to be tetragonal (space group *P4/mmm*; a = 3.734, c = 9.00 Å). All attempts by us to synthesize the tetragonal structure in bulk polycrystalline form have so far been unsuccessful. The tetragonal structure of $TlSr_2CuO_5$ reported by Kim *et al.* (*17*) is similar to other 121 cuprates like $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ (*8, 9, 20*), $TlSrLaCuO_5$ (*13, 14*), and $TlSr_2Cu_{0.4}Fe_{0.6}O_5$ (*16*). Figure 3 shows the structural model of orthorhombic $TlSr_2CuO_5$. The Cu–O sheet is planar and runs parallel to the (001) planes. Each Cu atoms is at the center of a distorted octahedron of oxygen atoms, which are corner-connected. Sr atoms are in ninefold coordination and lie above and below the Cu–O sheet. The Tl atoms (shown here in the idealized position) are in an octahedral coordination. In Table III we provide bond length data for some of these 121 oxides for comparison purposes. The most significant fact revealed from these data is the small Cu–O(4) bond length of 1.831 Å for the orthorhombic $TlSr_2CuO_5$. Assuming no oxygen vacancies, Cu should have the formal oxidation state of 3+. Cu–O bond lengths in other trivalent copper oxides are 1.850 Å in $NaCuO_2$ (*21*) and 1.840 Å in $KCuO_2$ (*22*). It is to be noted that the bond lengths of the $TlSr_2CuO_5$ (orthorhombic) phase have been calculated using an approximate model structure (Fig. 3).

In the above model, the Cu–O sheets are assumed to be flat; hence the Cu–O(4) bond length is half of the a-parameter. On the other hand, if the Cu–O(4)–Cu bonds are bent it is possible to have a larger (more reasonable) value of Cu–O(4) bond length. Bending of the Cu–O bonds leads to reduction of symmetry, and the space group can no longer be *Pmmm*, as assumed in our preliminary structural analysis. A more detailed structural study is necessary to sort out some of these issues.

Electrical resistivity measurements show $TlSr_2CuO_5$ to be metallic (Fig. 2). If this compound were to be stoichiometric, all the copper atoms should have the formal valence state of 3+ ($3d^8$, a non-Jahn Teller electronic configuration) and there would be two electrons in the σ^* (e_g) orbital (low

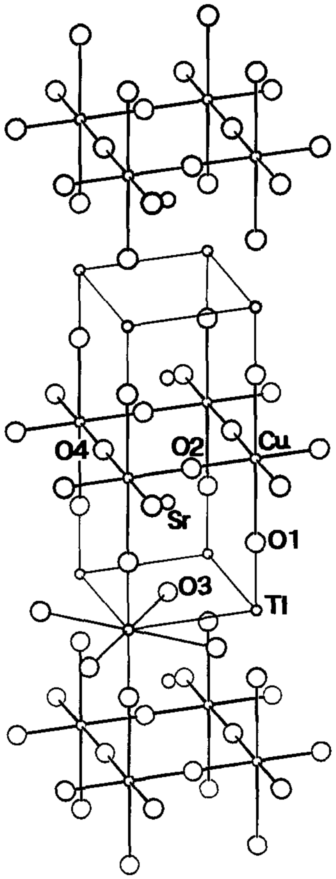

FIG. 3. Structural model of orthorhombic $TlSr_2CuO_5$.

spin); the metallic conductivity is probably due to the delocalization of e_g electrons. This situation is similar to $LaCuO_3$ which is metallic and has copper in the trivalent state (*23*). However, preliminary structural information from this study indicates that the structure of $TlSr_2CuO_5$ is very closely related to that of other 121-type cuprates with short in-plane Cu–O distances. It is likely that the formal valence state of copper in $TlSr_2CuO_5$ is below 3 and is compensated by oxygen vacancies. This situation is similar to the overdoped region of $La_{2-x}Sr_x CuO_4$ ($x > 0.3$), which also shows metallic behavior (*24*). Further studies on the oxygen stoichiometry and crystal structure are being undertaken to fully understand the mechanism of electrical conduction in $TlSr_2CuO_5$.

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