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Oxides of the Type $TlSr_2Cu_{1-x}M_xO_5$ (M = Fe, Co) Having the 121 Structure*

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Oxides of the type $TlSr_2Cu_{1-x}M_xO_5$ (M = Fe, $0.5 \leq x \leq 0.75$; M = Co, $0.3 \leq x \leq 0.5$) have been synthesized and characterized for the first time. These oxides were monophasic and crystallized in a primitive tetragonal structure (c-parameters ~9.0 Å. Lattice parameters vary systematically with x. All the oxides show semiconducting behavior. Neutron powder diffraction study on $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ shows structural features similar to those of other 121 oxides, but has comparatively less disorder in the Tl–O plane and has axially compressed Cu/Fe–O_6 octahedra.

Introduction

Thallium superconductors of the type $Tl_mCa_{n-1}Ba_2Cu_nO_{2n+m+2}$ (m = 1, 2) have been studied extensively in the last two years (*1*, *2*). Analogous Sr (in place of Ba) compounds could be stabilized by the substitution of Pb ($Tl_{0.5}Pb_{0.5}CaSr_2Cu_2O_7$, $Tl_{0.5}Pb_{0.5}Ca_2Sr_2Cu_3O_9$) (*3*, *4*) Bi ($Tl_{1-x}Bi_x Ca_2Sr_2Cu_3O_9$ and related oxides) (*5–7*), or rare-earth as in $TlCa_{1-x}Ln_xSr_2Cu_2O_7$ (*8*, *9*). All the above Sr superconductors contain single Tl–O layers (m = 1). It has been shown that similar substitutions led to the successful synthesis of Sr analogs of $TlBa_2 CuO_5$ (121) of the type $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ (metal) (*10*, *11*), $TlSr_{2-x}Ln_xCuO_5$ (T_c ~ 40 K) (*12*, *13*). In this communication we discuss the effect of substitution of transition metal ions (Fe, Co) at the Cu sites in an attempt to stabilize similar Sr containing 121 structures.

Experimental

Oxides of the type $TlSr_2Cu_{1-x}M_xO_5$ (M = Fe, Co) were synthesized by heating the component oxides (Tl_2O_3, SrO_2, CuO, Co_3O_4/Fe_2O_3) in the appropriate stoichiometry at temperatures ranging from 850 to 875°C for periods of 6 to 12 hr. All the reactions were carried out in sealed gold tubes. Powder X-ray diffraction with Cu $K\alpha$ radiation using a Scintag PAD IV diffractometer confirmed the monophasic nature of the oxides. Unit cell parameters were refined by a least-square fitting procedure. The possibility of superconductivity was checked by ac magnetic susceptibility studies. Electrical resistivity measurements were done on

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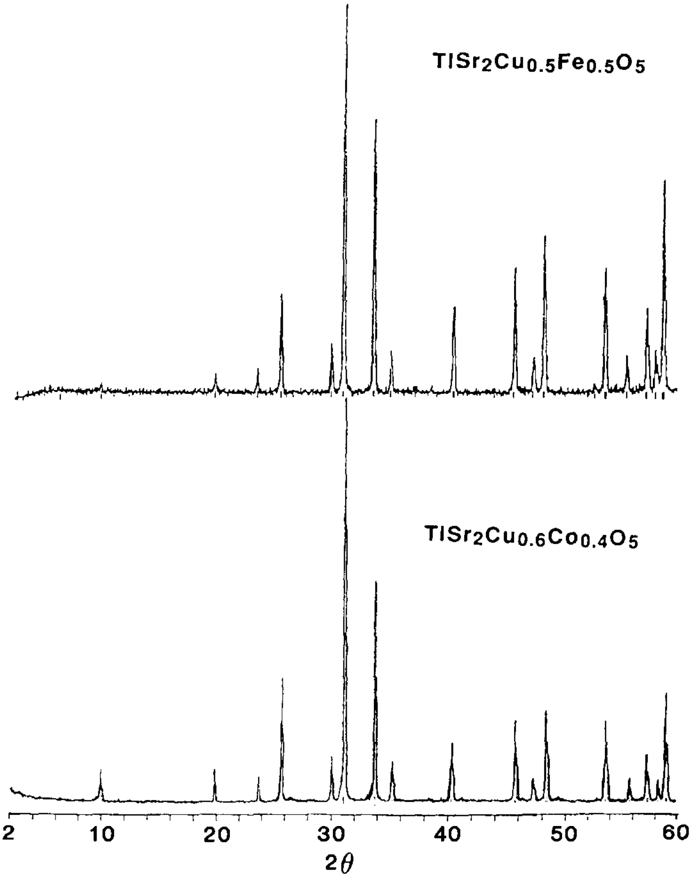

FIG. 1. Powder X-ray diffraction patterns of $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ and $TlSr_2Cu_{0.5}Co_{0.5}O_{5-\delta}$.

polycrystalline pellets using the standard four-probe method.

Neutron powder diffraction data for a 15-g sample of $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ at 300 K were collected on the high intensity powder diffractometer (HIPD) at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) at the Los Alamos National Laboratory. HIPD has an incident-neutron flight path of 9.5 m and a resolution Dd/d of 4×10^{-3}. Data were collected in four detector banks (at approximately ±153° and at ±90°) for approximately 2 hr at average proton currents of approximately 80 mA. The structural models were refined using the Rietveld refinement code developed by Larson and Von Dreele (*14*).

Results

In Fig. 1 we show the powder X-ray diffraction patterns of some of the oxides of the $TlSr_2Cu_{1-x}M_xO_5$ (M = Fe, Co) system. Monophasic oxides could be prepared for $0.5 \leq x \leq 0.75$ (M = Fe) and for $0.3 \leq x \leq 0.5$ for M = Co. Impurity lines were found for x values outside these ranges. The X-ray patterns could be indexed on a tetragonal unit cell (space group $P4/mmm$). The a parameter increases and the c parameter de-

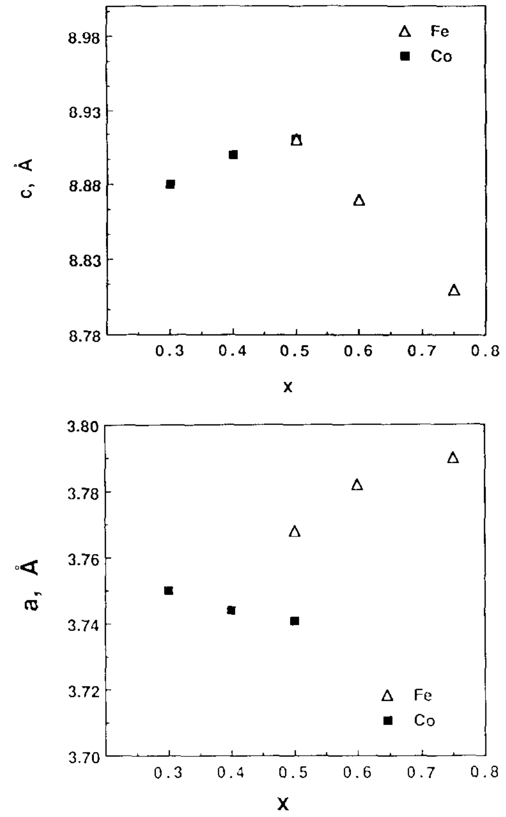

FIG. 2. Variation of lattice parameters (a, c) with composition (x) in $TlSr_2Cu_{1-x}M_xO_{5-\delta}$ (M = Fe, Co).

creases with x (M = Fe), as shown in Fig. 2. This variation in the lattice parameter is similar to that found in $Bi_2Sr_2Cu_{1-x}Fe_xO_y$ (*15*). By contrast, the a lattice parameter decreases and the c parameter increases in the case of Co-substituted oxides.

Magnetic susceptibility studies (by the ac mutual inductance technique) did not show a Meissner signal (down to 20 K) in any of the above oxides. Four-probe resistivity showed semiconducting behavior, with room temperature resistivities of $\sim 10^{-2}$ ohm cm.

Neutron diffraction data taken for $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ were indexed with the space group $P4/mmm$. The results for the structural refinements are given in Table I. In addition to the structural parameters shown, background, scale factor, absorption, extinction, and strain were also refined. Portions of the data and the fits are shown in Fig. 3. These show the quality of fit and the near absence of any impurity phases. A comparison of selected bond lengths for $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ (*16*) with those for the $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ is shown in Table II.

TABLE I

STRUCTURAL PARAMETERS FOR $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ AT 300 K

Parameter		Refined value
a(Å)		3.76941(3)
c(Å)		8.83992(12)
Tl	f	0.232(1)
	x	0.0676(5)
	U_{iso}	0.69(6)
Sr	z	0.28828(8)
	$U_{11} = U_{22}$	0.851(25)
	U_{33}	0.57(4)
Cu/Fe	f	0.391(2)/0.587(2)
	$U_{11} = U_{22}$	0.028(23)
	U_{33}	2.10(6)
O1	f	0.965(4)
	z	0.23708(11)
	$U_{11} = U_{22}$	1.31(4)
	U_{33}	2.14(7)
O2	f	0.996(4)
	U_{11}	0.27(3)
	U_{22}	0.63(4)
	U_{33}	1.63(6)
O3	f	0.232(2)
	x	0.4382(5)
	U_{iso}	1.11(9)
d spacing range		0.4–6.65 Å
R_{wp}/R_{exp}		3.73/2.56%

Note. Space group $P4/mmm$: Tl(x,x,0), Sr(1/2,1/2,z), Cu/Fe(0,0,1/2), O1(0,0,z), O2(1/2,0,1/2), and O3 (x,1/2,0). Units for thermal parameters are 10^{-2} Å^2. The numbers in parentheses following refined parameters represent the estimated standard deviations in the last significant digit.

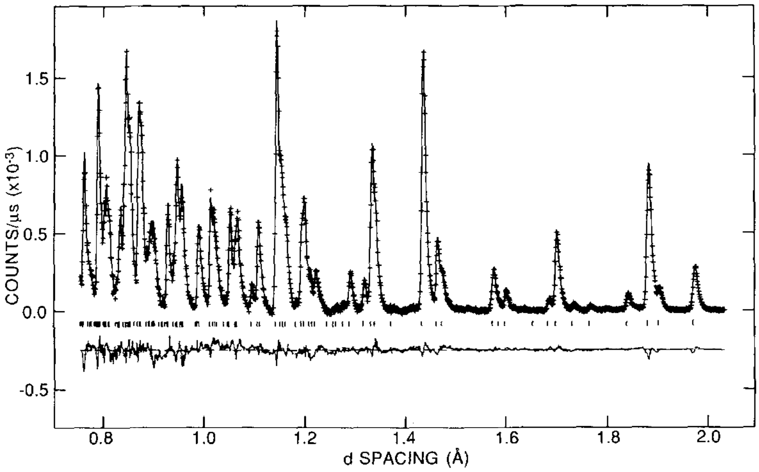

FIG. 3. Part of the neutron-diffraction data for $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$. Data shown by plus (+) marks are taken on the +153° detector bank of the HIPD at a sample temperature of 300 K. The continuous lines through the sets of points are the calculated profiles from Rietveld refinement. The sets of tick marks below the data indicate the positions for the allowed reflections. The lower curve represents the difference between observed and calculated profiles.

Initial fits with the Tl and O3 atoms located on the (0,0,0) and (1/2,1/2,0) symmetry sites, respectively, gave rise to large anisotropic thermal parameters in the a–b plane (approximately 0.050 and 0.089 Å^2, respectively) and to very small or negative values along the c-axis (0.004 and −0.003 Å^2, respectively). This behavior is commonly encountered in the Tl-based perovskites and has been attributed to short range ordering in the Tl–O planes (*16–18*). Accordingly, all four combinations of tetragonal displacements of the Tl from the symmetry position of the type (x,0,0) and (x,x,0), and of the O3 from the symmetry position of the type (x,1/2,0) and (x,x,0), were fitted (*16, 18*); none gave as good a fit (with weighted profile agreement factors, R_{wp}, ranging from 3.73 to 4.20%) as the fit with Tl and O3 on the symmetry sites (3.68%), but they all yielded more reasonable values for the (now isotropic) thermal parameters. As in the case of $TlBa_{1.2}La_{0.8}CuO_5$ and $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ (x,0,0) displacements for the Tl produced a slightly better fit [with O3 in the (x,1/2,0) site] than the (x,x,0) displacements; however, in contrast to the earlier studies where the choice of displacement model for O3 did not affect R_{wp}, displacements of the type (x,x,0) gave values of the agreement factor that were lower by 0.03%. However, these displacement models are only approximations to the actual disorder and should probably not be viewed too literally. As before,

TABLE II

COMPARISON OF SELECTED INTERATOMIC DISTANCES (Å) FOR $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$, AND $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ [16], ALL AT 300 K

Bond	$TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$	$Tl_{0.5}Pb_{0.5}Sr_2CuO_5$
Cu–O1	2.3242(10)	2.4914(7)
Cu–O2	1.88471(2)	1.8654(15)
Sr–O1	2.70436(19)	2.7177(3)
Sr–O2	2.6527(5)	2.6192(4)
Sr–O3	2.5744(8)	2.6837(6)
Tl–O1	2.1112(10)	2.0217(7)
Tl–O3	2.1632(27)–2.8202(28)	2.2236(19)–2.7509(18)

Note. The numbers in parentheses following the bond distances represent the estimated standard deviations in the last significant digit(s).

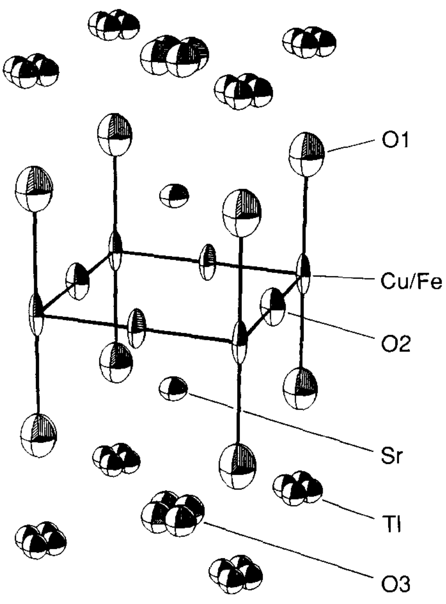

FIG. 4. The structure of $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ at 300 K. The anisotropic thermal parameters U_{11} and U_{22} for Cu/Fe were arbitrarily increased from 0.00028 to 0.002 Å^2 so that the thermal ellipsoids for Cu/Fe are more clearly visible. All thermal ellipsoids are drawn as 95% probability surfaces.

the absence of superlattice reflections in the diffraction patterns suggests that this ordering is of a short range nature.

As expected, anisotropic models for the thermal parameters for the displaced atoms resulted in unstable refinements; but anisotropic thermal parameters for the other atoms could be refined to give the values given in Table I. The thermal motions and static distortions of the constituent atoms in $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ are shown in the ORTEP plot (*19*) shown in Fig. 4. The overall structural picture closely resembles those for $TlBa_{1.2}La_{0.8}CuO_5$ and $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ (*16*, *18*). However, while the thermal parameters for the O1, which bridge the Tl/Pb and Cu in these two systems, exhibit large values in the *a–b* plane, presumably induced by disorder in the Tl/Pb–O3 layer, thermal parameters for O1 in $TlSr_2Cu_{0.4}Fe_{0.6}O_{5-\delta}$ do not suggest such large distortions. This, together with the much shorter Cu/Fe–O1 bond lengths, suggests a tighter coordination of the axial oxygen to Cu/Fe induced by Fe doping. The elongation of the thermal ellipsoid for Cu/Fe and O1 along the *c*-axis suggests that there may be some local disorder produced by differing Cu/Fe–O1 bond lengths when O1 is coordinated to Fe or to Cu.

Cu and Fe were assumed to occupy the same site in the 0.4 : 0.6 ratio fixed by stoichiometry. Occupancies for both Cu and Fe were refined to give values of 0.391(2) and 0.587(2), respectively, relative to the assumption that the Sr site is fully occupied. Refinement of the Tl and O3 occupancy led to values of 0.232(1) and 0.232(2), respectively, for the two fourfold sites. Oxygen occupancies for the O1 and O2 sites refined to 0.965(3) and 0.996(3), respectively. Thus, the overall stoichiometry of the sample can be represented by $Tl_{0.93}Sr_{2.0}Cu_{0.39}Fe_{0.59}O_{4.85}$, with an estimated accuracy of 1–2% for refined occupancies, and perhaps somewhat larger errors for occupancies of the fourfold sites. This produces a refined value of *d* of 0.15, and, if we assume an oxidation state of +3 for Fe, an effective oxidation state for Cu of +2.92.

Discussion

$TlBa_2CuO_5$ the prototype 121 structure has one Cu–O layer and one Tl–O layer. This oxide, though difficult to prepare as a pure phase, has been reported to be semiconducting (*20*). All attempts to prepare pure $TlSr_2CuO_5$ in polycrystalline form have so far been unsuccessful. Recently, it has been reported (*21*) that single crystals of $TlSr_2CuO_5$ could be obtained. Both $TlBa_2CuO_5$ and $TlSr_2CuO_5$ have all the Cu in the trivalent state. It is known that metal ions in their higher oxidation states can be stabilized in an oxide in the presence of highly electropositive elements (*22*). This may be the reason why $TlBa_2CuO_5$ is stable whereas $TlSr_2CuO_5$ is not (Ba being more electropositive than Sr). In the systems $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ and $TlSr_{2-x}Ln_xCuO_5$ reported earlier, Cu has a formal valence less than 3. In the $TlSr_2Cu_{1-x}M_xO_5$ (M = Fe, Co) system discussed in this paper, assuming the oxygen content to be close to five (as shown by neutron diffraction), it appears that trivalent Cu could be stabilized by disordering the Cu sites using other trivalent transition metal ions (Fe, Co). Another possibility is the presence of Fe^{3+}/Fe^{4+} or Co^{3+}/Co^{4+} in these oxides, leading to a formal valence state of copper less than 3+. The presence of Fe^{4+} has been detected by Mössbauer studies in $Bi_2Sr_4Fe_3O_y$ (*15, 23*).

In a related study, we synthesized oxides of the type $Tl_{0.5}Pb_{0.5}Sr_2Cu_{1-x}Fe_xO_5$ ($0.1 < x < 0.5$). These oxides have similar 121 structures as reported above and show systematic variation in their lattice parameters (a-parameter increases from 3.774 Å for x = 0.1 to 3.778 Å for x = 0.5; c-parameter decreases from 8.98 to 8.93 Å). All the oxides in the system exhibit semiconducting behavior. Since $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ is a metal (*10, 11*) it was of interest to investigate the metal–semiconductor transition for the possibility of obtaining new superconductors with the substitution of Fe at the Cu site. Unfortunately, substitution of minor amounts of Fe (x = 0.1) renders $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ semiconducting.

In conclusion, we have synthesized oxides of the type $TlSr_2Cu_{1-x}M_xO_5$ (M = Fe, Co) having the 121 structure in which Cu is likely in the trivalent state. Neutron diffraction study on one sample showed slight oxygen deficiency, leading to an effective Cu valence of 2.92. These oxides show semiconducting behavior. Detailed magnetic properties are currently being investigated by Mössbauer studies.

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