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$Tl(Sr_{1-x}Ba_xLa)CuO_5$: Superconductor–Semiconductor Transition via Isovalent-Cation Substitution

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Thallium cuprates $Tl(Sr_{1-x}Ba_xLa)CuO_5$ were synthesized and characterized. Single phases of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ can be obtained for all values of $x = 0.0$–1.0, and they crystallize in a tetragonal structure with space group *P*4/*mmm*. Both the *a* and *c* lattice parameters increase smoothly with increasing x, and $Tl(Sr_{1-x}Ba_xLa)CuO_5$ loses superconductivity for $x > 0.3$. These observations were explained on the basis of how the extent of overlap between the CuO_2 layer $x^2 - y^2$ and the Tl 6*s* bands changes as a function of the in-plane Cu–O bond length. © 1992 Academic Press, Inc.

For the superconductivity of the *p*-type cuprate superconductors, the presence of holes in their CuO_2 layers is essential (*1–5*). Holes may be generated by oxygen excess, cation vacancy, or substitution of cations with different valence (e.g., Sr^{2+} for La^{3+}), all of which are based on nonstoichiometry of the chemical compositions. There is yet another way of creating holes, as found for thallium cuprates (*5–8*). The latter are typically of the $22(n-1)n$ phases, $TlBa_2Ca_{n-1}Cu_nO_{2n+4}$, or the $12(n-1)n$ phases, $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. In the $22(n-1)n$ phases, the Tl–O double layers create holes in the CuO_2 layers via the overlap of the Tl 6*s* bands with the CuO_2 layer $x^2 - y^2$ bands. In contrast, the Tl–O single layers of the $12(n-1)n$ phases do not create holes, because the bottom of the Tl 6*s* bands lies above the Fermi level. This difference between the $22(n-1)n$ and the $12(n-1)n$ phases arises from the fact that the Tl 6*s* bands of the Tl–O single layers lie higher in energy than those of the Tl–O double layers, while the $x^2 - y^2$ bands of the $22(n-1)n$ and the $12(n-1)n$ phases are nearly the same in energy (*6*). The latter is a direct consequence of the fact that the in-plane Cu–O bond lengths are similar in the two phases (see below).

The $x^2 - y^2$ bands of the CuO_2 layers are antibonding between the copper and oxygen atoms in the in-plane Cu–O bonds (*5, 9, 10*). Thus, shortening of the in-plane Cu–O bonds, or equivalently the shortening of the *a* parameter, raises the $x^2 - y^2$ bands (*11*). If the in-plane Cu–O bonds of the $12(n-1)n$ phases are strongly shortened, the $x^2 - y^2$ bands are raised high enough to make the Fermi level rise above the bottom of the Tl

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6s bands and hence create holes in the CuO_2 layers. Such a modification of $TlBa_2CuO_5$, i.e., Tl(Sr*R*)CuO_5 (*R* = La, Nd) (*12, 13*), has been made by replacing the Ba^{2+} cations at the 9-coordinate sites with smaller cations Sr^{2+} and R^{3+}. According to the formal oxidation states Tl^{3+}, Sr^{2+}, and R^{3+}, one might expect a copper oxidation state Cu^{2+} in Tl(Sr*R*)CuO_5 (*R* = La, Nd), which implies no holes in the CuO_2 layers and thus no superconductivity for Tl(Sr*R*)CuO_5 (*R* = La, Nd). However, this phase is a superconductor because the $x^2 - y^2$ bands are significantly raised due to the very short in-plane Cu–O bonds (*11*). We note that an isostructural phase Tl(Ba*R*)CuO_5 (*R* = La, Nd) (*7, 8, 14*) is not a superconductor, most likely because the in-plane Cu–O bonds are not short enough (*11*).

The above discussion suggests that one can vary the extent of the overlap between the $x^2 - y^2$ and the Tl 6s bands of the 1201 phase, and hence the hole density in the CuO_2 layers, by substituting isovalent cations of different sizes (e.g., Ba^{2+} for Sr^{2+}). Since Ba^{2+} is larger than Sr^{2+}, the *a* parameter and the in-plane Cu–O bond length of $Tl(Sr_{1-x}Ba_xR)CuO_5$ (x = 0.0–1.0) should increase gradually with increasing *x* so that the $x^2 - y^2$ bands will be gradually lowered in energy as *x* increases. Then, $Tl(Sr_{1-x}Ba_x R)CuO_5$ should lose superconductivity beyond a certain *x* value. We show this to be the case by preparing and characterizing $Tl(Sr_{1-x}Ba_xLa)CuO_5$ as a function of *x*.

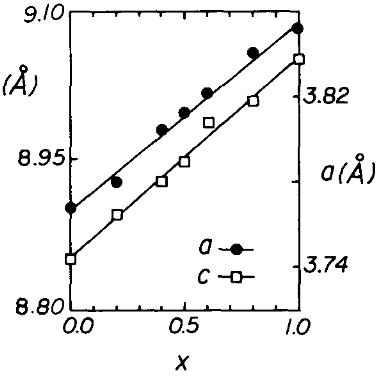

FIG. 1. Variation of the *a* and *c* parameters of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ as a function of *x*.

Samples of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ were prepared by heating stoichiometric amounts of Tl_2O_3, SrO_2, BaO_2, La_2O_3, and CuO in a sealed gold tube at 865°C for 12 hr and then cooling to room temperature in the furnace. Powder diffraction patterns were obtained using a Scintag PAD IV X-ray diffractometer, and the unit cell parameters were refined using a least-square procedure. Meissner effects were measured by the ac induction technique, and resistivities were measured by the standard four-probe method. Single phase samples of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ can be prepared for all values of x = 0.0–1.0. Powder X-ray diffraction patterns of the prepared samples were indexed on a tetragonal lattice with space group *P4/mmm*.

Figure 1 plots the unit cell parameters *a* and *c* of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ as a function of *x*. The *a* and *c* parameters increase gradually with increasing *x*, as anticipated. Table I summarizes the electrical properties measured for $Tl(Sr_{1-x}Ba_xLa)CuO_5$ as a function of *x*. Superconductivity is observed for samples with x = 0.0–0.3. This means that holes

TABLE 1

ELECTRICAL PROPERTIES OF $Tl(Sr_{1-x}Ba_xLa)CuO_5$

x	ρ at 300 K (Ohm cm)	ρ at 4.2 K (Ohm cm)	Comment
0.0	2.5×10^{-3}		$T_c \sim 42$ K
0.2	3.3×10^{-3}		$T_c \sim 44$ K
0.3	2.0×10^{-3}		$T_c \sim 37$ K
0.4	7.0×10^{-3}	6.5×10^{-3}	semimetal-like
0.5	5.6×10^{-3}	6.0×10^{-3}	semimetal-like
0.6	2×10^{-2}	1×10^{-1}	semiconductor
0.8	4	2×10^{2a}	semiconductor
1.0	1.3×10^{2}	4×10^{3a}	semiconductor

[a] Measured at 77 K.

are created in the CuO_2 layers due to the overlap between $x^2 - y^2$ and the Tl 6s bands for these x values. Samples with $x = 0.4$–0.5 exhibit nearly temperature-independent electrical resistivities. This semimetal-like behavior, expected for a semiconductor with very small band gap, suggests that the bottom of the Tl 6s bands lies only slightly above the Fermi level for these x values. Samples with $x = 0.6$–1.0 show typical semiconducting behavior. This shows that the $x^2 - y^2$ band is further lowered to produce a larger band gap for these x values. Furthermore, the resistivity ρ at a given temperature increases with x, which shows that the band gap of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ increases with increasing x. All of these findings reflect the facts that the $x^2 - y^2$ bands are antibonding between the in-plane copper and oxygen atoms, that the in-plane Cu–O bond length increases as more 9-coordinate sites are occupied by larger cations, and consequently that the extent of the overlap between the $x^2 - y^2$ and the Tl 6s bands decreases, due largely to the lowering of the $x^2 - y^2$ band, with increasing in-plane Cu–O bond length.

To summarize, the superconducting property of $Tl(Sr_{1-x}Ba_xLa)CuO_5$ is controlled by substitution of isovalent cations (i.e., Ba^{2+} for Sr^{2+}), because the in-plane Cu–O bond length is affected by the steric effects exerted by the 9-coordinate site cations. Our work shows that $Tl(Sr_{1-x}Ba_xLa)CuO_5$ loses superconductivity for $x > 0.3$.

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