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Superconductivity and the Metal–Semiconductor Transition in the Septenary Oxide System, $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$

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The septenary compound $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ exhibits the highest superconducting transition temperature (110 K) yet observed in the $TlCaBa_2Cu_2O_{7-\delta}$ (1122) structure type. This complex, six-blend combination of metallic elements which make up the material is, however, compensated by a relatively simply crystal structure, which bears many similarities to that of 90 K superconductor $YBa_2Cu_3O_{7-\delta}$. In this note we report some important features of the cation-substitution chemistry of the title compound, drawing attention to the fundamental changes in the electronic properties of the $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ system as Ca^{2+} is replaced by Y^{3+}. Superconductivity is observed over the homogeneity range $y = 0$–0.5, with the superconducting transition temperature showing a maximum (108 K) at $y = 0.2$. Across the homogeneity range $y = 0.6$–1.0, the material undergoes a metal–semiconductor transition. © 1990 Academic Press, Inc.

1. Introduction

The discovery of superconductivity in the Tl–Ca–Sr–Cu–O system (*1, 2*) has triggered intense research, aimed at both phase identification and improvements in the superconducting transition temperature, T_c. It now seems clear that substitution of Pb (*3–5*) or Bi (*6, 7*) in the Tl sites, or rare earth elements (La, Nd, and Y) in the Ca sites (*8, 9*), not only stabilizes the crystal structure of the phase responsible for high temperature superconductivity but also increases the volume fraction of superconductivity in the $TlCaSr_2Cu_2O_7$ phase (T_c = 80 K). With the substitution of Pb (*3*) or Bi (*10*) in the Tl sites, there is a concomitant increase in T_c up to 115 K in the $TlCa_2Sr_2Cu_3O_9$ phase. Recently, we have reported bulk superconductivity up to 110 K in the $(Tl_{0.5}A_{0.5})(Ca_{0.8}R_{0.2})Sr_2Cu_2O_{7-\delta}$ (A = Pb or Bi; R = Y or rare earth elements) system (*11–14*). This septenary system has the highest T_c among the thallium cuprate systems with the so-called 1122 structure (typical with $T_c \sim 80$ K), e.g., $TlCaBa_2Cu_2O_7$ (*15*), $(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_y$ (*3*), and $Tl(Ca,Y)Sr_2Cu_2O_y$ (*8, 9*). The thallium-based 1122 structure can be described in terms of an intergrowth of double rock salt-type layers $[(\{Tl/A\}O)(SrO)]$ with double $[Sr(Ca,R)Cu_2O_5]$ oxygen-deficient perovskite layers, formed by sheets of corner-sharing CuO_5 pyramids interleaved with calcium and/or

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rare earth ions. The structure of $(Tl_{0.5}A_{0.5})(Ca_{1-y}R_y)Sr_2Cu_2O_{7-\delta}$ resembles that of $YBa_2Cu_3O_{7-\delta}$: the (Tl, A)–O layers replacing the Cu–O chains, Sr atoms replacing Ba atoms, and Ca atoms partially substituting for rare earth atoms.

In this letter, we report the variation of the lattice parameters, room temperature resistivity, Cu^{3+} valence, and superconductivity on substitution of Y^{3+} ions for Ca^{2+} ions in the $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ system.

2. Experimental

Samples with the nominal composition of $(Tl_{1-x}Pb_x)CaSr_2Cu_2O_{7-\delta}$, $Tl(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$, $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$, and $(Tl_{1-x}Pb_x)Ca_{0.8}Y_{0.2}Sr_2Cu_2O_{7-\delta}$ were prepared as described previously (*13*). Briefly, high purity $CaCO_3$, Y_2O_3, $SrCO_3$, and CuO powders were calcined in stoichiometric proportions at 970°C for 12 hr in air to form a precursor. The precursor was then mixed with Tl_2O_3 and PbO, ground, and pressed into a cylindrical pellet, 10 mm in diameter and 2 mm in thickness, under a pressure of 2 tons/cm^2. The pellets were then wrapped in gold foil to prevent loss of thallium and lead during heating. The samples were then sintered at 950°C for 3 hr in flowing oxygen, followed by cooling to room temperature at a rate of 5°C/min or quenching in air. A microcomputer-controlled Philips diffractometer, equipped with a copper target and graphite monochromator for Cu$K\alpha$ radiation, was used to obtain the powder X-ray diffraction (XRD) patterns. The selected area electron diffraction (SAED) pattern was obtained on a JEOL-200CX electron microscope operating at 200 keV in which a ±45° double tilt stage was used. A standard four-point probe method was used for electrical resistivity measurements. The Cu^{3+} content was analyzed by iodometric titration (*16*).

3. Results and Discussion

All members of the solid-solution $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ $(0 \le y \le 1)$ have the 1122-type layered structure of $TlCaBa_2Cu_2O_7$ (*15*) with the *P4/mmm* space group. In Fig. 1, we show typical X-ray diffraction and electron diffraction (see inset) patterns of the monophasic $(Tl_{0.5}Pb_{0.5})(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$ sample. All the diffraction lines in the XRD or spots in the electron diffraction patterns for the sample could be indexed on the basis of a tetragonal unit cell having a = 3.803 and c = 12.067 Å.

Figure 2a shows the variation of the c lattice parameter with increasing yttrium content, y, in $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$. The reduction in c probably arises because the Y^{3+} ion (0.93 Å) is slightly smaller than the Ca^{2+} (0.99 Å) ion. Figure 2b shows the corresponding variation of lattice parameter a with y in $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$. We propose that this expansion in a is attributed to a decrease in the average copper oxidation state, leading to longer Cu–O distances within the copper oxygen sheets. A similar effect has been observed in $Bi_2(Sr_{3-x}Y_x)Cu_2O_{8+\delta}$ (*17*), $Bi_2(Ca_{1-x}Y_x)Sr_2Cu_2O_{8+\delta}$, and $Tl(Ca_{1-x}Y_x)Ba_2Cu_2O_{7-\delta}$ (*18*).

The compositional variation of the room temperature resistivity and Cu^{3+} concentration in the $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ system are shown in Fig. 3. Throughout the entire homogeneity range $(0 \le y \le 1)$, the room temperature resistivity increases with increasing yttrium content, y. By contrast, the Cu^{3+} concentration decreases with increasing concentration of yttrium. Both results, therefore, indicate that the "hole" concentration in these oxides can be effectively reduced by yttrium substitution for calcium.

In Fig. 4, we illustrate that the superconducting transition temperature $[T_{c(\text{zero})}]$ is affected by variations in either or both Tl : Pb and Ca : Y ratios in the systems (a)

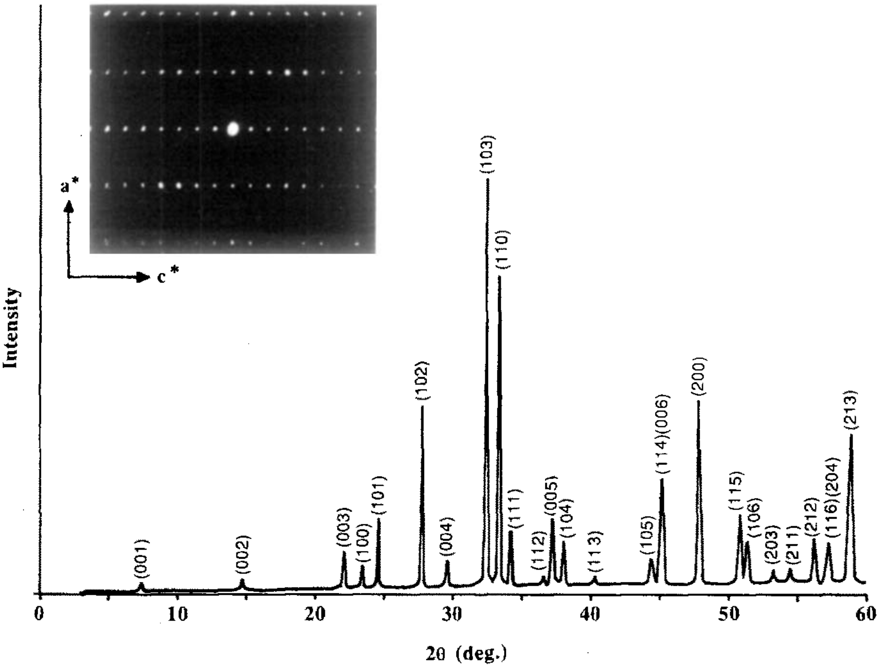

FIG. 1. X-ray diffraction and electron diffraction (see inset) patterns of the monophasic $(Tl_{0.5}Pb_{0.5})(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$.

$(Tl_{1-x}Pb_x)CaSr_2Cu_2O_{7-\delta}$, (b) $Tl(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$, (c) $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$, and (d) $(Tl_{1-x}Pb_x)(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$. In Figs. 4a and b, both the $(Tl_{1-x}Pb_x)CaSr_2Cu_2O_{7-\delta}$ and $Tl(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ systems have the highest $T_{c(zero)}$ of 78 K for $x = 0.5$ or $y = 0.7$. Figure 4c shows the variation of $T_{c(zero)}$ with yttrium concentration in the septenary system $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$. For $y = 0$, $(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_{7-\delta}$ is a superconductor with $T_{c(zero)}$ at 78 K and metallic (normal state) conduction as shown at $x = 0.5$ in the $(Tl_{1-x}Pb_x)CaSr_2Cu_2O_{7-\delta}$ compound (Fig. 4a). With increasing y, $T_{c(zero)}$ increases up to a maximum value of 108 K for $y = 0.2$, then decreases to 44 K at $y = 0.5$. For $y \gtrsim 0.6$, the sample exhibits semiconducting behavior. Recent specific heat measurements on the title system indicate that spin-glass behavior exists for the $y = 0.8$ sample (*19*). We propose here that the insulating state, $(Tl_{0.5}Pb_{0.5})YSr_2Cu_2O_{7-\delta}$, may, in fact, be antiferromagnetic (AFM). This proposal is based on (a) the absence of any intrinsic Cu^{2+} ESR signal from room temperature to liquid helium temperature, an observation reminiscent of high-temperature antiferromagnetic ordering in cuprates (*20*); and (b) the observation of antiferromagnetism in the related compound $TlBa_2YCu_2O_7$, which has a Néel temperature in excess of 350 K (*21*). Magnetic susceptibility studies are currently underway. Such a metal/superconductor-to-semiconductor transition with increasing y in $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ would place these septenary cuprate materials with other high-T_c oxide systems in which the interrelation between AFM and superconductor is now well es-

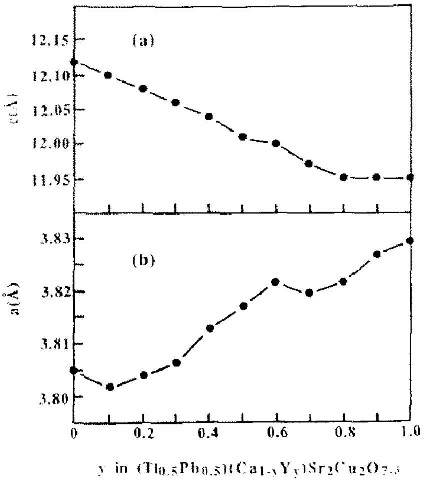

FIG. 2. The variation of the c lattice parameter (a) and the a lattice parameter (b) with increasing yttrium content, y, in $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$.

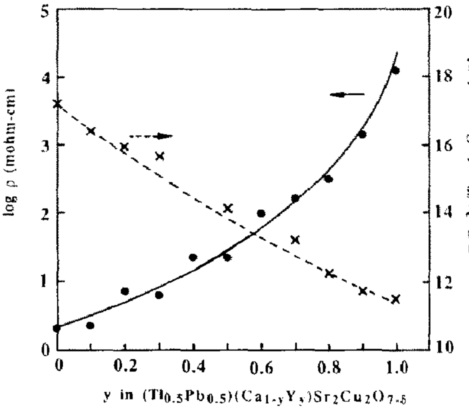

FIG. 3. The compositional dependence of the room temperature resistivity and Cu^{3+} concentration in the $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ system.

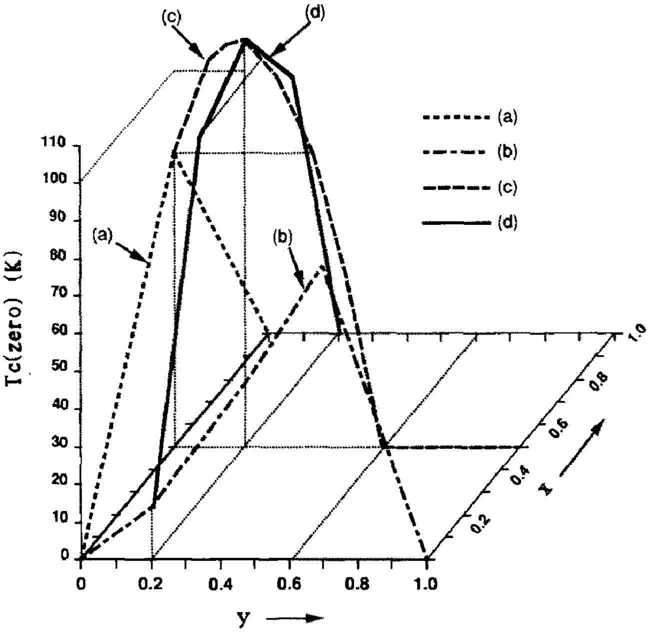

FIG. 4. Compositional effects of the superconducting transition temperature, $[T_{c(zero)}]$, with variations in x (Tl : Pb content) or y (Y : Ca content) in (a) $(Tl_{1-x}Pb_x)CaSr_2Cu_2O_{7-\delta}$, (b) $Tl(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$, (c) $(Tl_{0.5}Pb_{0.5})(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$, and (d) $(Tl_{1-x}Pb_x)(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$ systems.

tablished. These systems include $(La_{1-y}Sr_y)_2CuO_4$ (*22*), $YBa_2Cu_3O_{7-\delta}$ (*23*), $Bi_2[(Sr, Ca)_{3-y}Y_y]Cu_2O_8$ (*24*), and $Bi_2(Sr_{3-y}Y_y)Cu_2O_8$ (*17*). Figure 4d also shows a maximum $T_{c(zero)}$, up to 108 K, at $x = 0.5$ in $(Tl_{1-x}Pb_x)(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$. It is worth noting that the Tl : Pb ratio close to 1.0 is necessary to obtain the highest $T_{c(zero)}$ not only in the $(Tl_{1-x}Pb_x)CaSr_2Cu_2O_{7-\delta}$ system (Fig. 4a) but also in the $(Tl_{1-x}Pb_x)(Ca_{0.8}Y_{0.2})Sr_2Cu_2O_{7-\delta}$ system (Fig. 4d).

Recently, Hybertsen and Mattheiss (*25*) have suggested on the basis of band structure calculations that the Tl(Bi)–O sheets may act as a "hole reservoir," providing mobile hole carriers to the coupled Cu–O layers in the $\{Tl(Bi)_mL_2Ca_{n-1}Cu_nO_{2n+2+m}\}$ ($m = 1$ or 2, L = Ba, and $n = 1, 2, 3$ for Tl compounds; $m = 2$, A = Sr and $n = 1, 2, 3$ for Bi compounds). If this reasoning is correct, it means that the (Tl, Bi)–O sheets in these structures play the same role in the Cu–O chains of the $YBa_2Cu_3O_{7-\delta}$ compound. Once again, this highlights the similarities between the $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ and the $YBa_2Cu_3O_{7-\delta}$ system. Thus, chemical modification of the (Tl, Pb)–O coupling copper oxide sheets is expected to affect the superconducting properties of this material.

The results reported here indicate that the substitution of trivalent yttrium ions for divalent calcium sites in the $(Tl_{0.5}Pb_{0.5})(Ca_{1-y}Y_y)Sr_2Cu_2O_{7-\delta}$ system leads not only to a decrease in the effective hole concentration but also to an increase in the superconducting transition temperature [from 78 K ($y = 0$) to 108 K ($y = 0.2$)]. Such effects are consistent with the proposal that the parent compound, $(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_{7-\delta}$, is effectively "overcompensated," and a reduction in the Cu^{3+} concentration can now bring about an increase in T_c. We hope that the present experiments illustrate the high degree of control, and selectivity, of the electronic properties of these superconducting oxides. Such "six-blend" metal oxides, at first perplexing in their compositional variants, do appear to be particularly amenable to studying the composition-induced metal/superconductor to semiconductor transition (Fig. 4).

Acknowledgments

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