

Enhancement of the Superconducting Transition Temperature of $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ by Yttrium and Vanadium Substitutions

R. S. LIU AND P. P. EDWARDS

IRC in Superconductivity, University of Cambridge, Madingley Road, CB3 0HE, United Kingdom

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Superconductivity at 105 K has recently been observed in a family of compounds $(\text{Tl}_{1-x}\text{M}_x)\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_{7-\delta}$ ($M = \text{Ti, Zr, Hf, V, Nb, and Ta}$). An interesting feature is the enhancement of T_c in the parent $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ compound via substitution of high-valent 3d transition metals; this is in contrast to other high- T_c cuprates investigated so far. The effects on crystal structure and electronic properties of yttrium and vanadium doping in the metallic, but not superconducting, $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ compound are described. The new high- T_c superconductor, $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_{7-\delta}$, exhibits a current density of $1.5 \times 10^7 \text{ A/cm}^2$ at 5 K and 1 T for the sintered material which is comparable to that observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$. © 1991 Academic Press, Inc.

1. Introduction

Since the discovery of superconductivity in the La-Ba-Cu-O and Y-Ba-Cu-O systems, there has been extensive research on the substitution of 3d transition metals. Unfortunately, the incorporation of transition elements into these superconducting oxides always has a detrimental effect on the transition temperature, T_c (1). Recently, Doi *et al.* (2) have synthesized a monophasic $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ compound, which has single Tl-O sheets and tetragonal symmetry ($a = 3.7859 \text{ \AA}$, $c = 12.104 \text{ \AA}$; space group $p4/mmm$), but the material is not superconducting for temperatures down to 4 K. The authors proposed that the introduction of lead into $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ would optimize the hole concentration and lead to superconducting at high temperatures. In fact, Subramanian *et al.* (3) synthesized the compound $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CaCu}_2\text{O}_7$, which is superconducting below 80 K. In the case of the

$\text{TlSr}_2\text{CaCu}_2\text{O}_7$ compound, the Cu valence is $2.5+$, which appears to be too high and the compound is unstable and/or difficult to prepare as a single phase. Interestingly, a large number of 3d transition metal cations have accessible valencies of four and above. This aspect leads one to suggest that high-valent 3d transition metals might play the same role as lead ($4+$)—if they substitute for the Tl ($3+$) sites in $\text{TlSr}_2\text{CaCu}_2\text{O}_7$, rather than substituting in the Cu-O framework. If this is possible, the substitution would reduce the “overdoping” of $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ and give rise to a superconductor. This reasoning led to the synthesis of a new family of high- T_c superconductors in the system $(\text{Tl}_{1-x}\text{M}_x)\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_{7-\delta}$ ($M = \text{Ti, Zr, Hf, V, Nb, and Ta}$) (4-6).

Here, we report the results of an investigation of the substitution of thallium by vanadium in $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_{7-\delta}$ by a combination of electrical resistivity, magnetic, and X-ray diffraction measurements.

The aim is to obtain information on the role of vanadium in the Tl–V–Sr–Ca–Y–Cu–O system. In addition, we have measured the critical current density of this new high- T_c superconductor, $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_{7-8}$.

2. Experimental

Samples with nominal compositions of $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ and $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ ($0 \leq x \leq 0.7$) were prepared by mixing suitable amounts of Tl_2O_3 , V_2O_5 , SrO_2 , CaO , Y_2O_3 , and CuO , and forming a pellet, 10 mm in diameter and 2 mm in thickness, of this mixture under an applied pressure of 5 tons/cm². The pellets were wrapped in gold foil to prevent the loss of thallium at high temperature, then put into a tube furnace at 950°C for 3 hr (in flowing oxygen atmosphere). The samples were then cooled to room temperature at a cooling rate of 5°C/min.

A standard four-point probe method was used for the electrical resistivity measurements. The electrical contacts to the sample were made by fine copper wires with a conductive silver paint; the applied current was 1 mA. The temperature was recorded by a calibrated silicon diode sensor located close to the sample. Magnetization data were obtained using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). X-ray diffraction (XRD) studies were carried out with $\text{CuK}\alpha$ radiation using a Spectrolab CPS-120 diffractometer.

3. Results and Discussion

Using the preparation route described above, as-synthesized $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ is multiphasic (XRD pattern will be shown later). The sample exhibits metallic behavior from 300 to 4 K, except for a small electrical resistivity drop around 80 K, probably arising from a minority (<1%) supercon-

ducting phase (6, 7). Superconductivity in $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ can be induced by the replacement of 20% of the Ca^{2+} sites by Y^{3+} to give the compound $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ (8). However, the superconducting transition in $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ begins at 74 K, but zero resistance is not achieved until 15 K (see Fig. 1; $x = 0$).

The temperature dependence of the normalized resistivity for a series of samples of $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ is also shown in Fig. 1. Samples with nominal compositions $0 \leq x \leq 0.5$ exhibit metallic behavior in their normal state and an increasing T_c up to a maximum value of $T_{c(\text{onset})} = 105$ K, $T_{c(\text{midpoint})} = 100$ K, and $T_{c(\text{zero})} = 87$ K for the sample $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. For compositions above $x = 0.5$, the superconducting transition temperature decreases and the normal state resistivity appears to show semiconducting behavior.

In Fig. 2 we summarize the characteristic superconducting properties for samples of different vanadium composition in $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. The superconducting transition temperature [$T_{c(\text{midpoint})}$] increases from 47 K ($x = 0$) to 100 K ($x = 0.5$) and, at the same time, the transition width decreases. However, for x values above 0.5, the superconducting transition temperature decreases. In Fig. 2 we also show the compositional variation of the room temperature resistivity in $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. It is interesting that the room temperature resistivity increases from $x = 0.1$ to 0.7, which may be related to an effective decrease in the ‘‘hole’’ concentration in $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ via vanadium substitution (either V^{4+} or V^{5+} , see below) of thallium cations. This effect is similar to that found in the $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_y$ system, where substitution of Y^{3+} for Ca^{2+} results in a decrease in the hole concentration and an increase in the room temperature resistivity (9). However, we cannot rule out the possibility that this effect may arise from the presence of pyrochlore-type impurity

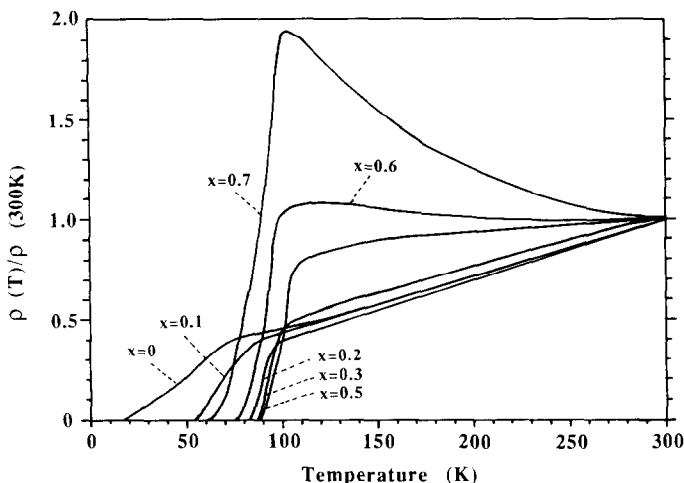


FIG. 1. The temperature dependence of the normalized electrical resistivity for a series of samples $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. ($x = 0$ up to $x = 0.7$)

phases when large amounts of vanadium are introduced into the $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ system.

In Fig. 3 we show the Meissner signals (field-cooled) for powder samples of $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ as measured

by a SQUID magnetometer in an applied magnetic field of 10 Oe. The magnitude of the Meissner signals increases from $x = 0$ to $x = 0.5$. At a nominal stoichiometry of $x = 0.5$, the sharpest superconducting transition (beginning around 105 K) was observed. With further increases in x above the value 0.5, the magnitude of the Meissner signals begins to decrease (Fig. 3). These magnetic data are in good agreement with the electrical resistivity results (Fig. 2).

In Fig. 4 we show the hysteresis loop at 5 K up to 5.4 T of the $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ sample. The intragrain critical current density, $J_{c(\text{intra})}$, has been estimated using the Bean model (10) based on the magnetization measurements. Assuming the grains are spherical, $J_{c(\text{intra})}$ values can be calculated by the formula (10):

$$J_{c(\text{intra})} (\text{A/cm}^2) = 30 \Delta M/d,$$

where ΔM (emu/cm^3) is the magnetization difference for the increasing and decreasing field sweeps and d is the average diameter (cm) of the grains. The intragrain critical current density at 5 K and $H = 1$ T for the $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ material was

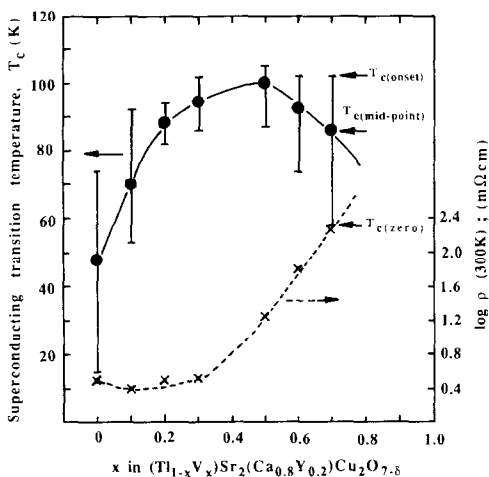


FIG. 2. The characteristic properties of superconducting transition temperature and room temperature resistivity for a series of samples with compositions of $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ (derived from Fig. 1).

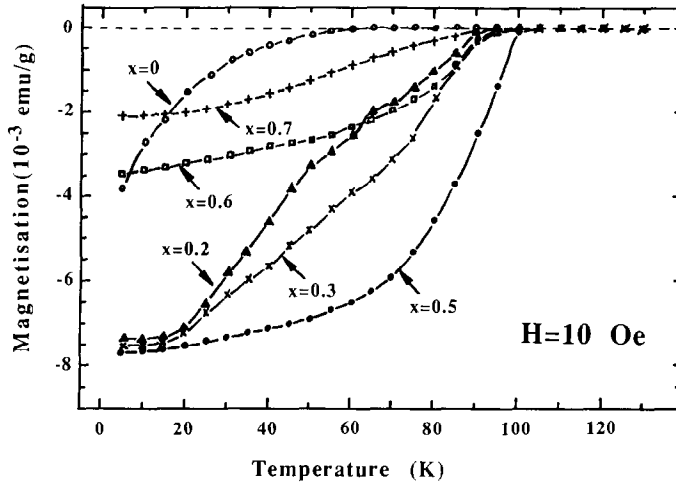


FIG. 3. Meissner signals (field-cooled) for powder samples of $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ measured by a SQUID magnetometer in an applied magnetic field of 10 Oe.

calculated to be $1.5 \times 10^7 \text{ A/cm}^2$ when a current loop size of $1 \mu\text{m}$ was used, which was estimated from a scanning electron microscope. This value is comparable with that of sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ (11).

In Fig. 5 we show the XRD patterns of samples with nominal compositions of $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ (a) and a series $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ ($x = 0, 0.2, 0.5,$ and 0.7 in samples b to e). Under our preparation conditions, the $\text{TlSr}_2\text{CaCu}_2\text{O}_y$

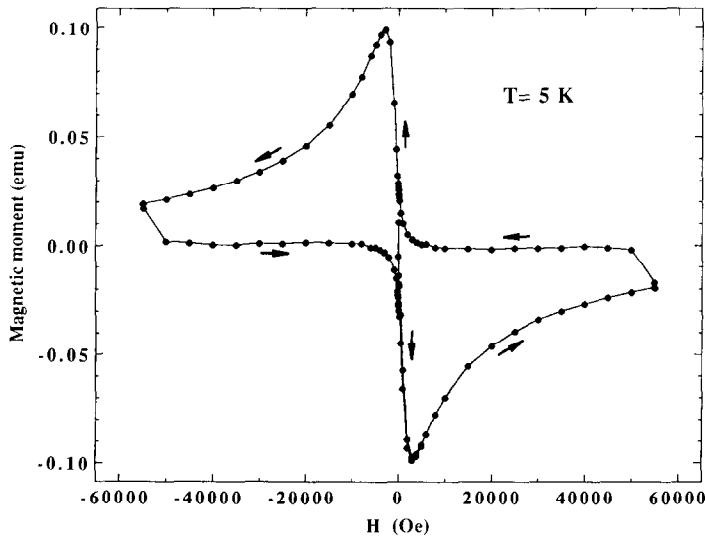


FIG. 4. Hysteresis loop at 5 K up to 5.4 T of the $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ sample (sample weight = 0.0687 g).

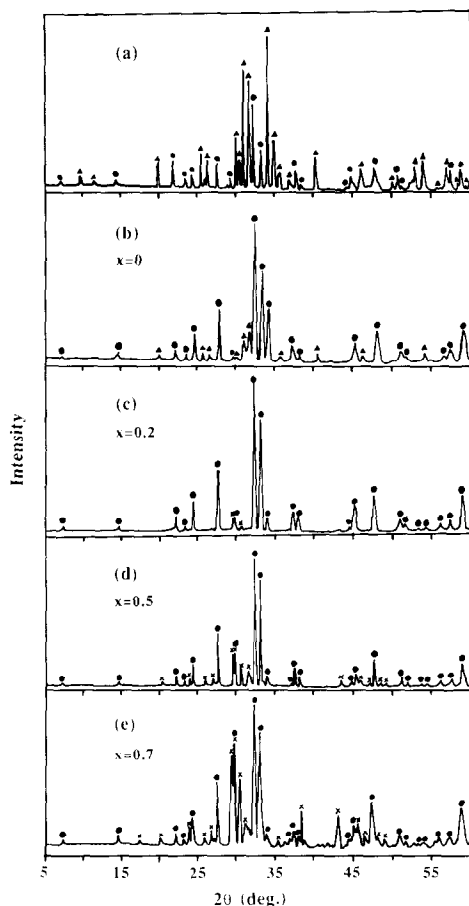


FIG. 5. XRD patterns of the nominal compositions of the $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ (a) and a series $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ ($x = 0, 0.2, 0.5,$ and 0.7) in samples b to e. (▲ and × represent the unidentified and pyrochlore SrVO_y -type impurity, respectively.)

compound is multiphase. One phase (indicated by ●) can be indexed on the tetragonal $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ phase (2). The concentration of the unidentified impurity phase (marked ▲ in Figs. 5a and 5b) in $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ can be reduced by ca. 20% of yttrium substitution into calcium in $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ [Fig. 5b]. Further substitution of 10–30% vanadium into the thallium sites results in a considerable reduction in the levels of the impurity phases in $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ [Fig. 5c].

Unfortunately, in addition to the vanadium incorporation into the thallium sites in $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$, we also have observed the formation of a pyrochlore SrVO_y -type impurity phase (6) (marked by × in Figs. 5c to 5e). This phase appears to always compete with the superconducting $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ phase for vanadium. This is illustrated in Figs. 5c, 5d, and 5e. From our previous electron energy dispersive X-ray spectrometry studies, it was shown that the actual chemical composition corresponding to a nominal composition $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ was, in fact, $[\text{Tl}_{0.71(6)}\text{V}_{0.27(4)}]\text{Sr}_{1.95(9)}[\text{Ca}_{0.86(7)}\text{Y}_{0.14(3)}]\text{Cu}_2\text{O}_y$ (6). Across the series of the $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ samples, the superconducting phase is based on the $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ -type structure and the c lattice parameters decreasing and the a lattice parameters expanding with increasing of vanadium concentration were also observed. These results suggest that the smaller V^{4+} (0.63 \AA) or V^{5+} (0.59 \AA) ions partially replace the larger Tl^{3+} (0.95 \AA) sites resulting in a decrease in the c lattice parameter. In contrast, we propose that the partial substitution of vanadium for the thallium leads to a decrease in the hole concentration in the Cu–O plane and a corresponding increase in the a lattice parameter. Measurements of the normal state magnetic susceptibility of this new high- T_c oxide system may help to evaluate the valence state of the vanadium ion.

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